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Since the time of Galilei 400 years ago the progress of optical systems was restricted due to the lack of optical glass types with different dispersion properties and due to poor material quality. With the work of Otto Schott, which started 125 years ago, glass became a tailorable, highly reproducible and homogeneous material, thus enabling systematic design of optical systems. The demand for new glass types is still going on as well as the requirement for ever tighter tolerances and their proofs. New measurement methods provide deeper insight in the material properties. Developments in processing allow new optical elements to be designed, further advancing technology. This also holds for zero-expansion glass ceramics, another key enabling material for optical systems. This publication highlights some milestones in the history of optical glass and glass ceramics, comments on present day glass development as well as new optical elements and measurement methods and provides some new information on the materials' properties. © 2010 Optical Society of America

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1. Introduction

Optical glass and glass ceramics are key materials not only for the optical industry but because of the high leverage effect of optical systems also for most research and development activities as well as for virtually all technology, i.e., in the end, for modern life in general. The use of optical glass not only changed our way of thinking initiated by Galileo with his discoveries but also the tremendous progress of medicine. Its life-lengthening effect, much of it coming from microscopic bacteria research and vaccination, would not have been thinkable without the availability of high quality, highly reproducible glass types with a full range of different properties. With the term optical glass we restrict ourselves in this article to those glass types that are produced by melting and are used for imaging and closely related applications. Other glasses, many of which are spin-offs from the classical optical glasses, have found their use in other high end technology such as information transmitting glass fibers, display glass, substrate glass, and fused silica. To outline their historical development and present status would go far beyond the scope of this publication.

In this publication we present some historical milestones in the development of optical glass and illustrate some of their most important influences. An outline of modern glass research follows: its new capabilities but also its restrictions and the present trends in the search for new glass types. Some selected new optical elements such as aspherical lenses, IR cut-off filters, micro-optical elements, and large glass disks are discussed to show the versatility of optical glass applications. Highlights in the progress of glass properties metrology are presented: the high accuracy refractive index and homogeneity measurement, the stress birefringence, and striae measurement.

Zero-expansion glass ceramic has found key applications in the optical world and now looks back on a long heritage of successful use in ground-based and space-based telescopes as well as in high precision industrial optics. Production methods have been improved. Significant progress has been made in

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gaining knowledge and control of the properties of the zero-expansion material Zerodur. Extreme homogeneity of the coefficient of thermal expansion has been achieved and proved. Tailoring of its absolute value is now possible, matching it to the thermal environment of the individual observatory. Further improved mirror light-weighting and expanded strength data support confidence in its suitability for future space applications.

2. Historical Milestones of Optical Glass Development

In the year 2009 we celebrate the 400th anniversary of the first scientific application of an optical instrument, the telescope, by Galileo Galilei. It had been invented shortly before by Hans Lippershey, an optician making spectacle lenses. Galilei built a series of telescopes with growing lens diameters from 22 mm to 58 mm and beyond with astonishing precision. Measurement of still existing lenses from this time in 1992 showed the quality of their spherical and flat surfaces, which is high enough to allow almost diffraction limited monochromatic images [1].

Also in 2009 there is another anniversary closely related to optical instrumentation. It was 125 years ago that Otto Schott, Ernst Abbe, and Carl Zeiss founded the company “Jenaer Glaswerke Schott und Genossen”. Schott introduced new optical glasses as well as new development and production processes, which allowed optics to become a technology. Now the design and reliable production of highly powerful optical systems became possible with far reaching consequences, which can hardly be overestimated [2].

The history of transmissive optical elements began with the invention of spectacle lenses at the end of the 13th century. Initially the use of crystals was common, as glass quality was still poor. Even though in the 15th century the glass makers of Murano, Venice, succeeded in removing the coloring, thus producing clear white glass, it took more than 100 years again until such glass was used for an optical instrument. It was the application by Galilei that made glass such an important contribution to the revolution in the development of science and also in the humanities as a whole. Besides his discoveries in astronomy he also proved the strategic importance of an optical instrument such as the telescope for defense. He demonstrated its capability to discover approaching ships much earlier than with the naked eye to the senate of Venice. This started the development of optical reconnaissance methods [3].

The restriction to only crown type glasses with little variations in refractive index and dispersion properties hindered the further development of optical instruments severely. Chromatic aberration limited any progress. This began to change when in the 1660s George Ravenscroft introduced lead oxide to the glass composition and found glass types with significantly different dispersion, the flint glass types. His intentions, however, were not optical applications but the production of bowls, goblets, and vases. Another 70 years later Chester Moor Hall and some time after John Dollond realized that the use of two glass types with different dispersion properties would lead to a strong reduction of the chromatic aberration. The resulting achromats, doublets made from a crown and a flint glass lens, should have caused rapid progress of optical systems, but poor glass quality restricted possible success. The glass was inhomogeneous and full of striae.

In 1805 Pierre Louis Guinand solved this problem. He introduced stirring into the glass melting process. This led to him being hired by the Bavarian entrepreneur Joseph Utzschneider, who operated an optical institute and wanted to get a reliable source of high quality optical glass. One year later Joseph Fraunhofer also joined the institute. In 1807 glass production started at the workshop in the monastery Benedictbeuern in Bavaria [4].

Fraunhofer was the first to improve optical glass manufacturing on a scientific and technological basis. He studied the influence of composition on glass properties and achieved much lower absorption losses. He was the first to characterize the optical properties of his glasses with physical measurement methods. On his search for wavelength calibration references he found the absorption lines in the solar spectrum, the Fraunhofer lines. Finally he succeeded in producing lenses with 28 cm diameter of high quality. This enabled him to build the leading astronomical telescopes of his time. However, the untimely death of Fraunhofer in 1826 disrupted further progress in optical glass, which would have been significant enough to enable substantial improvements of optical instruments. The knowledge and skill of optical glass melting gradually died out in Germany.

Stimulated by Fraunhofer’s success Michael Faraday entered the field of optical glass melting in 1825 and demonstrated the advantage of melting in platinum crucibles. From 1830 on William Vernon Harcourt made extensive investigations on widely varying glass compositions. He introduced many newly discovered chemical elements and also used other glass network formers than silicates. However, these achievements did not lead to the establishment of optical glass production in England with new glass types other than the already known crown and flint glass types. Faraday had stopped his experiments before obtaining technically usable glasses and Harcourt’s trial melts were too inhomogeneous to allow characterization of their optical properties. Additionally high taxes on all glass melting in England at that time prevented systematical process development for new glass types [3].

For about 60 years the production of optical glass was concentrated at two companies, one in France and one in England. Part of Fraunhofer’s heritage found its way via the Guinand family, who established a glass melting company in Paris, France named Feil and Guinand, subsequently changing to Parra-Mantois, Sovirel, and finally to Corning France.

In 1848 the head of the glass production workshop, Georges Bontemps, went from Feil and Guinand to the company Chance Brothers in Birmingham and helped to establish optical glass manufacturing there, which became first Chance Pilkington and finally Pilkington Special Glass.

At the end of the 19th century the German optical industry complained about the limited availability of optical glass. There were only the two suppliers, Feil and Chance Brothers, both outside Germany. The glass quality varied greatly and German companies received only the low quality melts if any at all. This was also a strategic problem because the supply with optical reconnaissance instruments was endangered [5].

Additionally the manufacturing methods for microscopes were unsatisfying. For many years they had depended on trial and error. The resulting optical quality was not predictable. Carl Zeiss, who was operating the Jena University optical instruments workshop at that time, was unwilling to simply accept this situation. So he asked the optics expert Ernst Abbe if he could help him with the design of high quality microscopes. Abbe's analysis led to the finding that the main obstacle was the lack of high quality glass types with considerable differentiation in their dispersion properties.

This was the time when Otto Schott, a descendant of a family with a long tradition in sheet glass manufacturing, entered the history of optical glass. He had made trial melts in a small laboratory in the house of his parents on his own initiative and expenses. The glass samples he sent to Abbe led to an invitation to Jena to start a glass laboratory there. Here the high skills of the systematically working chemist Otto Schott combined in an ideal way with the measurement and optical design capabilities of Ernst Abbe and the instrument building capabilities of Carl Zeiss. Otto Schott received not only theoretical but also practical feedback. This was an optimal environment to develop a whole set of glass types within very short time [2].

The new glass types were published together with conventional ones, which now were specified more precisely, in the first catalog of the "Glastechnisches Laboratorium Schott & Gen Jena" [6]. Schott was the first to be capable of melting chemically durable glass types with high reproducibility in those properties that high end optical systems require: refractive index, dispersion, transmission, optical homogeneity, and low content of bubbles, striae, and stress birefringence. He turned optical glass into a technical material, which means a material that is precisely specified and reproducible in its properties. Moreover he established methods to calculate glass properties from compositions before the glass was melted. This opened the way to systematic development of new glass types.

Now having a reliable set of materials available optical design could start its success story. Microscopes with highly improved resolution and color reproduction enabled revolutions in the progress of medicine [7]. Infectious diseases could be investigated in detail and vaccination methods were developed thus leading to many years of lifetime being added to hundreds of millions of humans since then. High quality optical glasses are still key materials for optical technologies, which are key enablers for all industries today.

The development of optical glass types progressed rapidly and many spin-off glass types made their way into other applications such as gas light cylinders out of heat resistant borosilicate glass for lighting city streets at the end of the 19th century.

The critical importance of optical glass was revealed again in a pronounced way in World War I, when France, England, and the U.S. were cut off from the optical glass supply in Germany. In a very short time the company Chance Brothers in England had to increase their glass output by up to a factor of 18. In the USA first production of optical glasses were started by Bausch & Lomb and later by NBS, Corning, and Pittsburgh Plate Glass [8].

In the 1930s the landscape of optical glass types was enlarged again. George Morey discovered the outstanding optical properties of lanthanum-containing glass types. These glasses combine high refractive index with comparatively low dispersion and good transmission in the blue-violet spectral range. The company Eastman Kodak developed a set of seven glass types in this area [9]. Shortly after World War II Walter Geffcken of Schott extended the range of lanthanum glass types even farther in the high refractive index and low dispersion range. Lanthanum-containing glass types are used nowadays in almost every optical design in consumer and high end optical systems.

New lead-borate glass types with deviating partial dispersion were introduced in the 1950s (KZFS-Glasses) and shortly after that extreme fluorophosphate glass types (FK, PK glass types) as their optimal partners for best color correction [10].

Glass development still continues today, steadily challenging the limits of the Abbe diagram, mostly set by crystallization of the melts instead of forming a glass. Many of the glass types with extreme optical properties can be produced only because special methods have been identified to prevent crystallization. Developing even more extreme positions requires compositions which crystallize so rapidly, that it is currently not possible to get a glass cast.

In 1954 S. Donald Stookey of Corning Glass Works made a serendipitous discovery. The accidental overheating of a lithium-containing photosensitive glass did not lead to deformation of the sample as should have been expected. Also its breakage strength turned out to be much higher than that of ordinary glass. A new class of materials had been discovered: glass-ceramics [3].

The most pronounced property of glass-ceramics is their low or even zero thermal expansion. Intensive studies showed that these materials could be produced reproducibly in a two-stage process, first melting a glass and after that a controlled growth of tiny crystals called ceramization. The composition has to provide nucleation agents to enable the formation of crystal nuclei. For controlled ceramization the material-specific temperature regimes for nuclei formation and crystal growth have to be clearly separated. The low thermal expansion property opened the path to much better astronomical mirrors and to extremely precise and thermally stable structures such as scales and frames required in the development of microlithography. Again as in optical glass development a main application of glass ceramics was identified outside of optics in cook top panels.

Another great advancement was to make glass ceramic items very large and thick but still conserving their homogeneity. The coefficient of thermal expansion depends on the temperature versus time program, which is applied to a glass ceramic item during ceramization. For thick pieces of glass ceramic, which is a very low thermal conductor and which additionally releases energy during crystal growth, it is very difficult to avoid strong temperature gradients, which would lead to different properties in different parts of the total volume.

In the early 1970s Jürgen Petzold of Schott succeeded in casting a 3.9 m diameter and 0.8 m thick mirror blank [11]. Since then the glass-ceramic Zerodur has found many applications in astronomy and high end optics especially where highest material homogeneity and reproducibility of properties are essential [12].

In the 1990s the gradual development of new glass types was strongly accelerated by the request for lead- and arsenic-free optical glass types. Glass suppliers had to change their glass programs thoroughly and rapidly. The Japanese company Hoya was the first to offer only lead- and arsenic-free glass types. Ohara of Japan followed some time later, and Schott had widely changed its program by the end of the 1990s but still kept some lead- and arsenic-containing glass types in the program, the reason being that for special high end optical instruments the unique combination of high refractive index, partial dispersion, and especially high transmission in the near ultraviolet spectral range of lead flint glass types is indispensable. If these glass types would be not available anymore this would mean severe drawbacks, for example, for fluorescence microscopy, a key optical method used in medical research, diagnosis, and therapy. For 7 years now the German optical industry under the lead of the industrial federation Spectaris and supported by Carl Zeiss, Schott, and many other important companies all over the world has fought against state regulations that would forbid these glass types with negative consequences for health, research, safety, environment protection, and technological progress. The debate resulted in a preliminary victory with a temporary exemption of lead glass types in 2005, but it has not been finally resolved.

Progress has been made not only in glass development but also in data representation and metrology. In 1992 Schott introduced a new function describing the dispersion of optical glass with higher precision. The Laurent series used up to this point was a formula taken from mathematics without a derivation from physical principles. It could lead to deviations of dispersion in the ranges between the sampling points used for parameter fitting. The Sellmeier formula introduced, however, is based on general dispersion theory and has been thoroughly investigated for high precision. Deviations from the true dispersion curve lie in the low single digit 10^{-6} range [13,14].

In the 1990s optical glass manufacture and metrology was pushed to its very limits. Microlithography changed from using g-line (436 nm) to i-line (365 nm) wafer steppers. The progress in resolution required not only shorter wavelength but also extreme optical glass quality. All properties had to be kept in much narrower tolerances. The glass disks to be produced in Mainz, Germany, with more than 200 mm diameter and about 50 mm thickness were much bigger than those used for conventional high end optics. Refractive index and dispersion variations were twice as narrow as the usual narrowest tolerances for large batches of disks. Transmission at the wavelength used had to be as close to 100% as possible because all absorbed light leads to temperature inhomogeneity of the lenses and thus optical inhomogeneity. The disks were virtually free from bubbles and inclusions. Stress birefringence was kept around 1 nm/cm and below, with wavefront deformations caused by striae significantly below 10 nm for total disk thickness and optical homogeneity better than $4 \cdot 10^{-7}$ over diameters of typically 240 mm. This number refers to the peak-to-valley value. The values for Zernike polynomial terms lay significantly below. This had to be achieved not just for single pieces but for thousands. Melting, measurement, data processing, and administration processes had to be improved significantly. Several preconditions were necessary to achieve this. Due to the high amount of glass required the production runs were long enough that they could be optimized and stabilized. Process monitoring computers allowed direct control. The refractive index measurement method based on the V-block principle, which was just introduced at that time, combined accuracy in the 10^{-6} range with low cost and high throughput. A 500 mm aperture Direct 100 interferometer just put into operation, provided high spatial resolution and much higher wavefront measuring accuracy in the single digit nanometer range. Originally this instrument was not bought for microlithography purposes but for homogeneity measurements in general. But as soon as it went into operation it had to be pushed to its very limits. Working around the clock is not common for such instruments. Additional investments had to be made in order to achieve high throughput of samples together with best possible temperature homogeneity management. Finally temperature variations could be kept below 0.05 K throughout the resonator cavity for many hours [15]. Even though the demand for *i*-line glasses dropped sharply in 1997, it has not died up completely until this day, as many semiconductor circuits do not require highest resolution but highly economic production.

The process improvements also benefitted conventional glass production with improvements in homogeneity and other quality characteristics. This could be demonstrated for example by casting large optical glass disks from N-FK5 and LLF1 with outstanding optical homogeneity.

A major trend in optical glasses that was initiated by Hoya more than 20 years ago, which has become more pronounced in the past 10 years, is the development or qualification of glass types suited for precise pressing. This means producing lenses from preforms such as polished balls, disks, or from glass gobs with fire-polished surfaces by pressing them to their final shape at comparatively low processing temperature, conserving the highly smooth surface. This eliminates the need for further polishing. Only centering and antireflection coating have to be added to have a lens ready for mounting. This process allows mass production especially of aspheric lenses, a prerequisite for advancements in high quality digital still and video cameras with high image quality. Precise pressing is most important in consumer optics, which uses mostly small and thin lenses, as the annealing after pressing can only be done in the press mold itself and must be fast in order to be economic. Larger and hence thicker lenses would suffer from stress birefringence and inhomogeneity if produced in the same way.

The precise pressing trend led to all glass suppliers' now having a program of glass types that are suited or specially developed for this production method. The main requirement for the glass types is that they can be plastically deformed at lowest possible temperatures (the glass-specific transformation temperature should be below approximately 550 °C) so that the expensive press forms have lifetimes long enough for the overall process to be economic.

From the days of Otto Schott the number of available glass types has steadily grown up to a peak in the 1960s (see Fig. 1) The slight decrease in the 1970s and 1980s was followed in the 1990s by a sharp decline. The expanding variety resulted from the goal of having the best glass type for each individual application. However, in the 1990s manufacturers realized that this led to increasing complexity and because of the low quantities requested of many glass types also to an unfavorable economical situation for such glasses. So together with the introduction of eco products the total number of glass types was drastically reduced either officially in the catalog or by restricted availability of melts for small quantities.

The discussion among optical designers about the minimum number of optical glass types required ended with the conclusion that in principle about

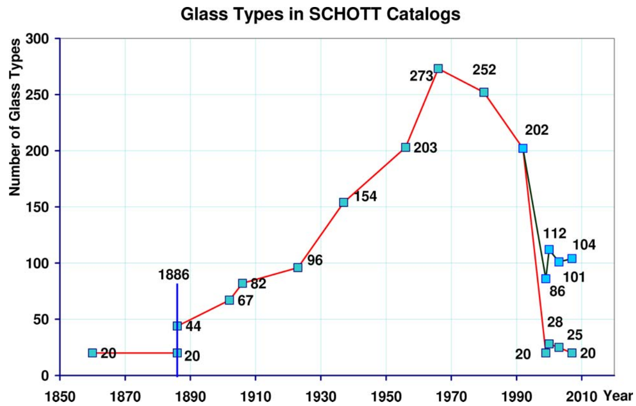


Fig. 1. (Color online) Number of glass types in the Schott catalogs since the first edition in 1886. Before there were around 20 types available. In 1999 classical glass types dropped to 20, whereas the total amount summed up to 86 including the new lead arsenic free glass types.

40 should be sufficient for most systems [16]. However, the designers of different companies could not agree on a specific set of glass types. Each company has a unique heritage of designs, which are the basis of new designs. A radical change would lead to unbearable costs. The changes to the glass programs in the past decade led many designers to feel insecure about the long term availability of specific high quality glass types. This is especially important for high end and defense optics, because here designs often have lifetimes significantly exceeding ten years. Suppliers have responded and are trying to establish confidence with a variety of measures. For example Schott issues a list of glass types that are guaranteed for at least the next 5 years and abandons a glass type only due to low demand. After the announcement of the glass type's removal from the program it will still remain available for 5 years. However, the general trends in optical design make it increasingly difficult to maintain an economically healthy glass portfolio:

– Replacement of glass lenses by plastic lenses (spectacles, DVD pick-up lenses, mobile phone cameras).
– Replacement of two or more spherical lenses by one aspherical lens.
– Smaller glass parts and near net shape glass parts (precision pressings).
– Combination and miniaturization of optical elements.
– Replacement of glass by mirrors or electronics (e.g., penta prisms of SLR cameras).

Optical glass will still be needed in the future without doubt. The historical importance for research and technology remains unchanged, and so optical glass will remain a key material for the future development of society. But its existence should not should not simply be taken for granted. Pilkington Special Glass went out of business in 2006 and Corning

France does not actively offer their glass types any more. Both companies seem to have missed developing their own lead- and arsenic-free glass types. It might be that the amounts of glass sold did not justify the necessary high investments. Schott is the last remaining optical glass manufacturer in the Western world and the only one who takes care of the interests of the optical companies with respect to EC environmental regulations, endangering optical glass availability, a problem that in the end will spread all over the world. In their purchasing policies optical companies should not optimize solely on the basis of cost but also on the long term existence of their key suppliers.

3. Modern Optical Glass Types: Development Trends

A. Glass Developer's View

We have already illustrated that within a comparably short time frame, the landscape of the material class "glass" has changed completely. Starting from silicate-based glasses, now nearly all oxides of stable elements in the periodic system can be used to obtain glass. Many glasses today contain no silicate-based network at all, and some of them are not even formed from oxides, but instead contain halides, chalcogenides, or even nitrogen as counter ions in the network.

These developments were enabled by optimizations in production technology: noble metal crucibles, stirring, and annealing (= controlled cooling) of the glass melt and—most importantly—the availability of all types of raw materials in very high purity grades.

For all optical glasses except filter glasses, color or absorption bands are not desirable. Natural raw materials contain a variety of impurities, leading to typical discolorations. Modern production methods guarantee impurity levels of a few parts in 10^6 (ppm) only, allowing ultrahigh transmittance qualities for example the high transmission grade "HT", or the *i*-line glass types for lithography.

Some of these impurities absorb not just visible light but also UV light. In many cases UV absorption results in emission of fluorescence light in the visible range of the spectrum. For applications such as fluorescence microscopy, these luminescence effects have to be suppressed as much as possible. Besides raw material quality, the melting process itself has to be controlled, to avoid coloration or haze coming from scattering at tiny inclusions. Depending on melting conditions, polyvalent ions can change from the colorless state to the colored one. For example depending on the surrounding matrix tungsten can be colorless or dark blue. Polyvalent ions can also form colored complexes in the glass matrix. Even high purity noble metal crucibles can lead to coloration of the glass. Yellowish color may result from tiny platinum particles, brown tint from rhodium in platinum-rhodium alloys, or gray from iridium particles in the glass.

Just as the glass landscape has changed, the process of glass development has as well. Historically glass development was mainly based on experience as well as on trial and error using mainly well-known silicate-based composition systems. Compared to other solids, glass has the advantage, that its properties can be changed gradually by changing the batch composition. Of course there are some limits in achievable properties and also in glass-forming composition ranges, however, this behavior allows tailoring of optical materials with special property combinations.

As glass properties can be described as the sum of influences of each component, statistical design methods are now widely applied for the design of new glass types. These methods are also necessary to handle the increased number of components in modern glasses. Ten or more different oxides are the rule now rather than the exception. Additionally a high number of properties have to be modeled. However, the statistical methods are restricted, certain concentration ranges have to be chosen narrow enough to ensure a linear dependence of the property on the concentration of the component. With an iteration process influence factors can be obtained for each component, which allows calculating the optimum composition for a given set of properties.

Of course, there is more than one combination of components that would at least theoretically lead to the desired target glass. However, not all of these compositions lead to a glass at all. Here the experience of the designers is needed again [17].

For optical glass, the most important properties from the view point of optical designers are of course refractive index and dispersion of refractive indices. To present a quick overview of available optical positions, i.e., $n_d - \nu_d$ combinations, optical glass companies usually use the so-called Abbe diagram, e.g., like the Schott Abbe diagram in Fig. 2.

In an Abbe diagram, the refractive index n_d of a glass is plotted against its Abbe number ν_d, where the subscript d denotes the Fraunhofer d-line at the wavelength of 587.6 nm. The Abbe number ν_d is a measure for the dispersion of a glass and is defined by

$$\nu_d = \frac{n_d - 1}{n_F - n_C}, \qquad (1)$$

where n_F and n_C are the refractive indices at the F line (~486.1 nm) and the C line (~656.3 nm). The higher the Abbe number, the lower the dispersion, i.e. the lower the wavelength dependency of the refractive index.

The Abbe diagram is divided into various sectors, so-called glass families, which are historically defined by the type of chemical composition of the glass types in this area. Thus, initially designers and manufacturers of optical systems had known from the composition which kind of chemical system they are dealing with—an important information for many postprocessing steps, especially such as grinding (e.g., hardness, abrasion) or polishing and

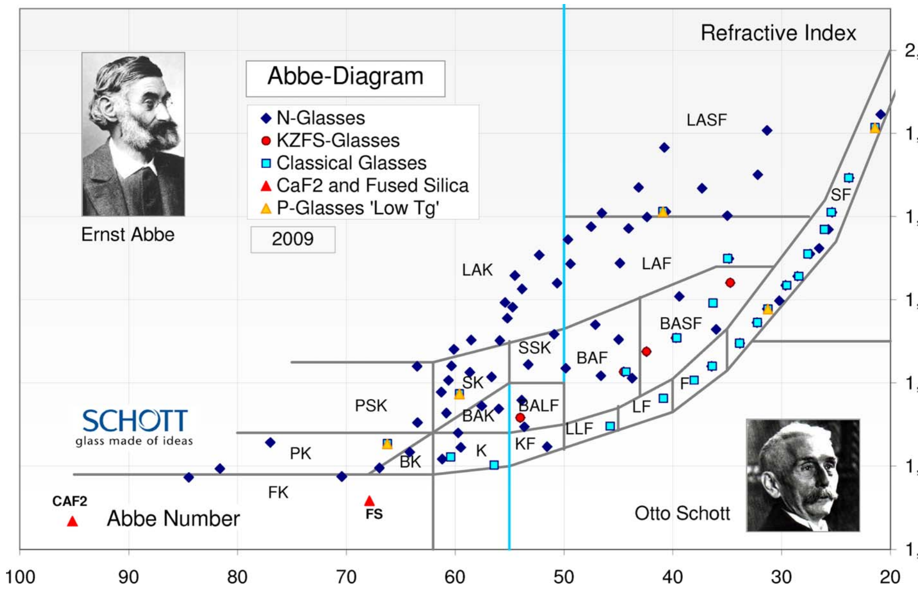


Fig. 2. (Color online) Abbe diagram of SCHOTT's glass portfolio. Photos: Schott.

cleaning (chemical resistance, climate resistance). Nowadays, the chemical glass systems widely overlap. So just from looking at the optical position range, more than one chemical system would be possible.

Looking at the large selection of components that can be used for glass development, one would expect never-ending possibilities for $n_d - \nu_d$ combinations. This is true within the inner part of the glass island in the Abbe diagram. Glass island here means the part of the diagram area that is covered with the dots representing glass types. However, the island has edges. The main reason for the restriction and the shape is closely connected to the dependence of the optical position on the composition of a glass. The general rule for shifting the optical position of a glass can be described as an increase of n via increasing the microscopic polarizability α^D (see Fig. 3). It can be either increased by decreasing the volume (thus increasing the density) or by increasing (some of the) α_i:

$$\alpha^D = \frac{\sum_i \alpha_i}{V}. \tag{2}$$

V (volume, α_i) can have different components:

α_{atom}—atomic polarizability,

$\alpha_{e\text{-}h}$—excitation of electron-hole pairs,

α_{vib}—excitation of IR lattice vibrations (of minor importance).

The first strategy (see Fig. 3) increases n_d without changing ν_d that much. On first thought, this would be the optimum method to achieve the desired combination of high n_d and high ν_d. However, there is one problem: increasing the density by decreasing the volume would lead to more dense packing of the atoms in the network. Increasing the package density inevitably leads to a more ordered structure, as would be typical for crystals—and thus further to ceramics than to the desired glass (this is the reason for the so-called "magic line" for glasses).

The second strategy, increasing alpha, implies use of heavy ions, having larger atomic polarizabilities as well as smaller bandgaps. High ν, however, would further require a large bandgap. Applying this strategy would shift the optical position to the upper right corner of the Abbe diagram, towards the high dispersion end (this is the reason for the bent shape of the glass area).

There has been a some success in proving that certain glasses can be formed within the typical crystal range by applying the first strategy, however, as long as those glasses cannot be economically produced in larger sizes or hot formed, they should be regarded as oddities rather than real commercial products.

Along the edges of the glass island $n_d - \nu_d$ combinations are restricted due to the fact that not all possible combinations of components results in a glass—even under extremely fast cooling. Other combinations will not even melt under normal conditions, which means that pots can still be used.

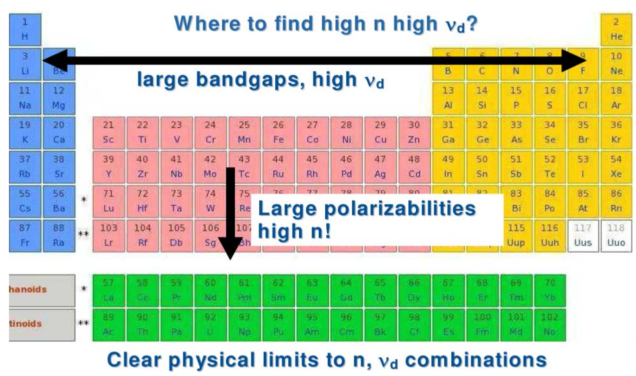


Fig. 3. (Color online) Basic chemical design strategy to develop glass in certain optical positions in the Abbe diagram.

The interest in very special glass types led to extreme production conditions, which cannot be controlled in high volume fabrication sufficiently. For instance, extremely short cooling rates have to be applied to obtain rare earth aluminates, glasses consisting mainly of rare earths, such as lanthanum oxide or zirconium oxide and aluminates. Their optical positions in the Abbe diagram can be found far away from the typical glass range, in an area, usually covered by crystals (see the red double arrow in Fig. 4). Other examples would be barium titanates, with low ν_d but refractive indices above 2.1. Both material systems are melting at high temperatures and have strongly crystallizing compositions, which leads to two problems: where to melt, as most crucible types are either thermally or chemically instable, and how to cool quick enough. For the first, so-called containerless melting methods, such as laser melting or mirror furnace melting have been developed (e.g., at 3M, ClZ, AT&T). For the second, small melt volumes have to be used, such as thin films and tiny spheres by plasma spray or flakes by rolling through cooled twin rolls.

Other glasses that have to be fabricated under extreme conditions are the nonoxide glasses. Nitride glasses have to be molten under oxygen exclusion and by applying high pressure (HIP-process). The raw materials of typical chalcogenide glasses first have to be distilled to remove oxidic "contaminations" and then also be made molten in an autoclave to avoid contact with oxygen or air, which could lead to explosions.

Some of the chalcogenide glass types, such as arsenic sulphides and selenides, germanium–arsenic–selen or germanium–antimony–selen systems, have already made their way into volume fabrication and optical applications such as IR cameras, night-vision systems, etc. (Vitron IG types). Also several fluoride glasses, with ZBLAN as the most prominent member, are already well-known commercial glasses. In contrast, nitride glasses and rare earth aluminates are still in a developmental state, as high volume fabrication of larger piece sizes is not possible or economically profitable. Nevertheless, research in these areas goes on, because enabling volume fabrication of those glass types would in a sense fulfil designers' dreams.

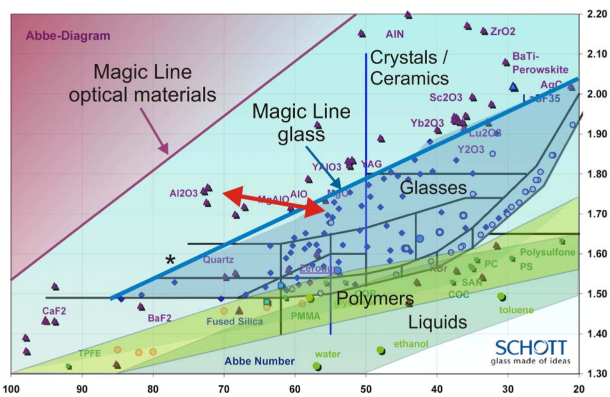


Fig. 4. (Color online) Abbe diagram, highlighting areas, where material types (crystals glasses, polymers, and liquids) can be found. The red double arrow marks the optical positions of rare earth aluminates, obtained e.g. by laser melting.

B. Optical Designer's View

SCHOTT offers a broad variety of optical glasses, as shown in the Abbe diagram Fig. 2. All these different glass types are necessary to achieve good optical performance. The refractive power $1/f$ of a lens is proportional to $(n-1)$ [18] $1/f \sim (n-1)$, where n is the refractive index of the lens. Thus an increase in the refractive index from 1.5 to 1.7 increases the refractive power by 40% due to the $(n-1)$ term. Spherical aberration—a monochromatic aberration—is proportional to $1/n^2$ [19,20]. Therefore high index glasses $(n > 1.8)$ ensure a high refractive power of the lens and reduce the monochromatic aberrations. In addition the high refractive power reduces the curvature of the lens which in turn reduces the monochromatic aberration as well as the weight of the lens. Unfortunately the increased refractive index reduces the transmission of the glass at about 400 nm ("blue-violet transmission") and below. This is a fundamental relation since the refractive index rises only in the vicinity of absorption lines, which also leads to higher slopes, i.e., higher dispersion. There is no way around this. High purity raw material and optimal melting process can only avoid additional losses and thus make the UV-edge steeper. However, for thin lenses the blue-violet absorption may be low enough to be acceptable. The designer must decide where a high index glass can be used or if a glass with lower refractive index should be used instead.

In addition to monochromatic aberrations, color aberrations (chromatic aberrations) exist that result from the wavelength dependence of the refractive index. In order to compensate color aberrations glasses with different Abbe numbers are needed, which together form the simplest correction element, the so-called achromate, bringing blue and red light into the same focus. A classical achromate consists of two glasses with an Abbe number difference of about 30, such as N-BK7 $(n_d = 1.5168, \nu_d = 64.2)$ and N-SF2 $(n_d = 1.6477, \nu_d = 33.9)$.

In order to further compensate the chromatic aberration glasses must be used with a dispersion curve different from those of common glass types. This deviation is characterized by the partial dispersion, e.g., in the blue-violet range $P_{g,F,}$ which is defined by

$$P_{g,F} = \frac{n_g - n_F}{n_F - n_C}, \qquad (3)$$

with the refractive indices of the glass at the F-line (~486.1 nm), g-line (~435.8 nm), and C-line (~656.3 nm), respectively. As a rule of thumb glasses that deviate from the normal line, which is defined by the classical glass types BK7 and F2, are needed to further reduce the chromatic aberration. The $P_{g,F}$ versus ν_d diagram is shown in Fig. 5.

Five major trends can be defined in optical design: 1, high n_d; 2, high ν_d, as the optimum the combination of both; 3, high n_d and high ν_d; 4, high n_d and low ν_d; and 5, the use of Low Tg glass types.

4. Design Trend 1: High $n_d > 1.7$

The high refractive power of the glass can be used not only to reduce spherical aberration but also to shrink the dimensions of lens systems. Looking at the "slim fit" or miniaturization trend for "pocket cameras," mobile phone cameras with optical zoom, etc., it is obvious why high n_d glasses are more and more replacing polymer optics: it is still not possible to achieve high n_d in polymers without severe scattering, haze, or low solarization stability. High n_d glasses can be found among the SF- and LASF-Types (e.g. N-LASF35, N-SF66). There is also a selection of so-called low-Tg glasses available in this area in the Abbe diagram, which allows low cost and high volume fabrication of aspherical lenses for consumer optics. All these types are difficult to produce, due to their sensitivity to coloration.

5. Design Trend 2: High $\nu_d > 60$

Low dispersion glasses, such as phosphates, fluorophosphates and fluorides (PK-, FK- types, e.g., N-PK51, N-PK52A, N-FK51, N-FK54), are widely used for optical systems with very high requirements on low chromatic aberration. They find their ideal partners in the KZFS glass types. Nearly all of those glasses have a low Tg and most of them have been qualified to be used for precision molding. However, low dispersion glasses have some problematic properties: they have high coefficients of thermal expansion (CTEs) and are relatively soft and chemically unstable. This makes them difficult to produce in high quality and requires a protective coating against humidity.

6. Design Trend 3: High n_d and High ν_d

Such a material would be the dream of every designer and have an extreme impact on optical designs. The unique combination of high refractive power and low chromatic aberration would allow efficient color correction in small dimensions (fewer lenses, lighter weight).

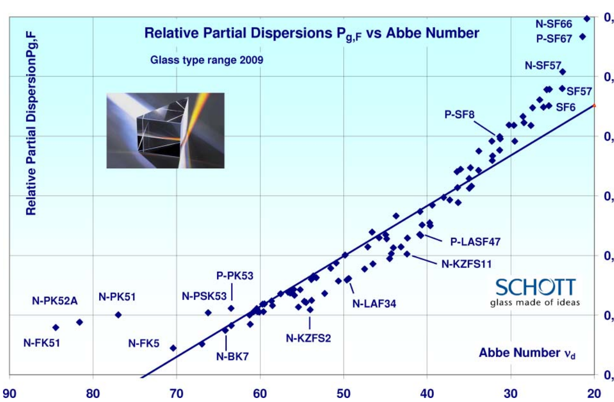


Fig. 5. (Color online) $P_{g,F}$ vs. n_d diagram of SCHOTT optical glasses. The straight line is the so-called normal line.

Recently opto-ceramics have been developed as isotropic optical materials with optical positions extending into the high n_d–high ν_d range. Though some very first products using opto-ceramic lenses exist, these materials have several drawbacks: they are still extremely difficult to produce and have high hardness, which leads to very high fabrication costs for lenses. Further, only certain compositions are possible, so there is no way to tailor this material. Additionally, the small but still present grain boundaries of most opto-ceramics act as scattering centers leading to stray light and hence intensity and contrast loss.

It has been possible to extend the glass range into the crystal range, but those materials have too high T_g and melting temperatures plus an extremely high crystallization tendency. Until now from a practical or commercial point of view there has still been no solution found in this area, but research continues.

7. Design Trend 4: High n_d and Low ν_d

A new trend employs ultrahigh dispersion glasses with Abbe number $\nu_d < 20$ for color correction as one of the achromate partner glasses. The glass FDS-18 from Hoya has an Abbe number of $\nu_d = 18.0$, and a partner glass could be N-KZFS4 with Abbe number $\nu_d = 44.5$. This concept differs from "conventional designs". Usually partner glasses would have to be in the LAK or LASF-range instead of, e.g., FK or PK. Typical glass systems for "ultrahigh dispersion glasses" would be niobium phosphate or certain bismuth-germanate systems. The biggest problem with those glasses besides their high batch costs is still the restricted blue-violet transmittance.

Camera software nowadays can compensate for some color imperfections. However, current image chips still have one major drawback: their weak sensitivity in the blue range of the visible spectrum. This requires that red and green channels have to be reduced in intensity to fit to the weaker signal of the blue channel. In difficult light situations such as early dawn, late evening, or bad weather, the signal-to-noise ratio and the resulting image quality become extremely bad. Thus, designs using color correction by high dispersion concepts could lead to low contrast and bad image quality. Therefore many producers of optical systems still prefer the traditional concepts.

8. Design Trend 5: Low T_g Glass Types

The high price pressure for certain optical products, especially consumer products such as compact digital cameras, is reflected in the increasing interest in low T_g glasses, where T_g stands for the glass-specific transformation temperature. Here the principle of molding polymer optics has been transferred to glass. For glass as an inorganic material with strong atomic bonds, molding and especially precision molding is not that easy. There is long experience in pressing of glass at low viscosity resulting in changes to the surface texture of the glass items. Surfaces have to be ground and polished to achieve exact shapes and sufficient optical quality. For precision molding much higher viscosities are used in order to conserve surface smoothness.

Precision molded optics require highly accurate molds usually made from tungsten carbide or silicon carbide with different types of coatings. Platinum- or carbon-based coatings serve to avoid glass sticking or reactions between the glass and tungsten carbide. The precisely fabricated molds are the most expensive part in precision molding. Its lifetime decides whether a lens can be produced economically.

The widely used tungsten carbide molds are quite sensitive to oxidation at higher temperature. Further, those molds typically use cobalt as binder, which could diffuse into the glass in the case of direct contact and lead to surface colorations. This is the main reason for the increasing interest in glasses with $T_g < 500$ °C and especially $T_g < 450$ °C. On the other hand, the same weak molecular networks, that enable T_g to be that low are also chemically more instable. These glasses show lower resistance against acids, caustics, and humidity. Thus, the lower the T_g the higher the need to apply protective coatings, especially when using phosphate-based glasses. Typical glass systems for low T_g types are lanthanum-zinc-boron, niobium-phosphorus (bismuth), bismuth-boron, tellurium-zinc, tellurium-phosphorus, or lead-silicon types.

Cleaning is also difficult: there are already polishing and cleaning steps in preform fabrication. The same surfaces are often cleaned a second time just before precision molding. Leaching of soluble components can have an influence on the surface quality of the pressing. During precision molding the surface composition of the glass can change once more because of evaporation. The glass is cleaned again and then coated. At the time of coating as a worst case the surface composition of the glass can differ strongly from the bulk composition, with possible negative consequences for optical quality and adhesion of the coating. Additionally condensates might form on the mold surface, shortening the lifetime of the expensive molds. Therefore one cannot assume that each catalog glass with a low T_g is directly suited for precision pressing, they have to be qualified. Also new glass types have to be developed to broaden the variety of optical positions taking into account their stability against evaporation at molding temperatures from the very beginning.

9. Optical Components: Imaging

Optical systems consist of various components such as lenses and filters. Traditionally spherical lenses have been used because they can be produced with low or moderate effort. Aspherical lenses or in short aspheres with at least one surface deviating from the spherical shape are the better components, but in the past their production was extremely difficult and costly. With the introduction of precise pressing aspheres were more and more important since now they have become available in high quality at relatively low costs. This holds at least for small dimensions. Larger diameters are possible via the magneto-rheological fluid polishing process. Figure 6 shows a typical design of a digital camera lens system with 4 aspheres and an optical filter.

The aspheres are manufactured from low T_g glasses using the precise pressing process. The glass is heated up as a polished preform. Then it is pressed using the mold to its aspherical shape. Finally the asphere is cooled down rapidly to stabilize the shape.

Due to the mass manufacturing process by precise pressing and the performance benefit aspheres are widely used nowadays. The performance benefit of aspheres comes from the reduction of monochromatic aberrations (e.g., spherical aberration). The reason for monochromatic aberrations is the nonlinearity of the Snell's law of refraction with respect to the angle: $n_1 \sin(\alpha_1) = n_2 \sin(\alpha_2)$. Aspheres compensate for this nonlinearity with their adjusted deviation from the spherical shape. However, they can reduce only the mononchromatic aberrations. To compensate chromatic aberrations one still needs different glass types.

10. Glass Filters

A digital sensor for photography is used for the wavelength range between approximately 400 nm and 650 nm but has its highest sensitivity at 1100–1300 nm. In order to ensure a good signal-to-noise ratio the IR part must be blocked by an IR cutoff filter, which lets the visible light pass through and blocks the IR light.

There are mainly two types of optical filters: coated filters employing the interference effect and glass filters, which are colored by different means: ionic absorption or semiconductor microcrystals. With coated filters spectral transmission curves can be tailored in a wide range with steep edges. But they strongly change their characteristics with the light incidence angle. Glass filters do not have such steep edges, but their filter characteristics are almost independent of the light incidence angle. Moreover they provide higher light-blocking factors than coated filters. One can also use a combination of both methods, coated colored glass filters. The application of filters is widespread in metrology and illumination.

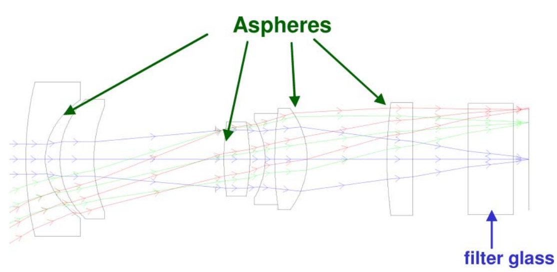


Fig. 6. (Color online) Optical design of a digital camera with 6 lenses (4 of them are aspheres) and an optical filter. After [39].

11. Nonimaging Optical Components

A new application of aspheres is the collimation of LED light. In Fig. 7 a 5 mm diameter aspherical glass lens can be seen. The LED is an extended source (typical emitting area of 1 mm × 1 mm), which has to be to be considered during the optical design.

For the design shown in Fig. 7 a low T_g glass with refractive index 1.80 (P-LaSF47) was used. The high refractive index together with the aspherical shape ensures a good collimation. Such aspheres can be realized as single lenses and also as an array of lenses. See Fig. 8, where a lens array with only 1.55 mm diameter lenses is shown.

A new form of micro-optical components can be realized in glass: diffractive optical elements (DOEs). DOEs use the wave nature of light and diffract light into the desired shape [20]. One application of DOEs is as a beam shaper, where a Gaussian beam of a laser is shaped into a rectangular—the so-called flat hat—shape; see Fig. 9.

Flat hat beam shaping DOEs are designed with a special design software and afterwards realized by precise pressing into glass. Details can be found for example in [20]. Measurement results of a glass DOE can be seen in Fig. 10.

Compared to polymers glass DOEs offer the benefit of highly reproducible microstructures, high laser durability, low scattering losses, and high resistance to moisture, chemicals, and temperature.

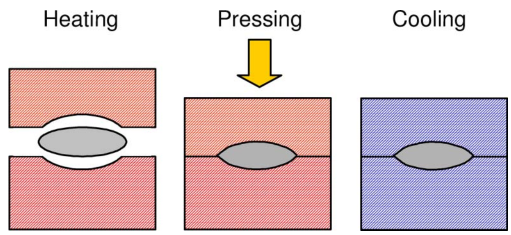


Fig. 7. (Color online) Sketch of the precise pressing process. First step: heating of the glass preform. Second step: pressing of the preform into the desired shape. Third step: cooling.

12. Large Items of Optical Glass

At present projects for extremely large telescopes (ELTs) are proceeding with increasing speed. Additionally to the telescope mirrors, transmissive optics are needed with large optical elements for beam shaping, atmospheric dispersion correctors, and wave band filters. Even though large transmissive lenses and prisms have been produced in the past this is still a challenge especially with increased quality requirements. Typical for large optical transmissive elements are the reduced set of possible materials and their long delivery time, which can easily reach one year. If additionally metrology development should be necessary the delivery time might surpass even two years. In order to provide optical elements with the required sizes and qualities in time for the completion of the telescopes the developments have to be addressed as early as possible [22]. In recent years the capability to produce large disks of optical glass with outstanding quality has been demonstrated repeatedly. However, since this is not a continual business it is not easy to conserve the high skills needed for such glass items.

13. Measurement of Optical Glass Properties

Optical glass as a technical material requires well-defined reproducible properties on which a designer

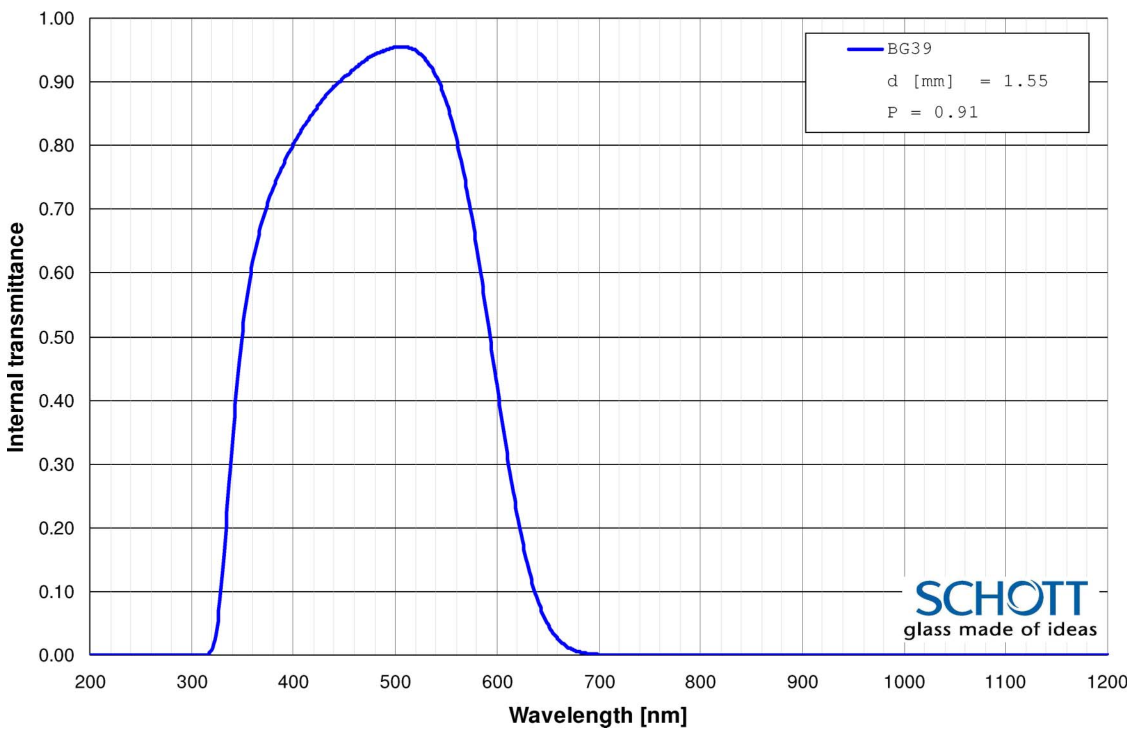


Fig. 8. (Color online) Filter characteristic of SCHOTT's BG39 absoprtion filter, which can be used as an IR cut filter.

Fig. 9. (Color online) Optical design of a LED collimation lens (diameter 5 mm) with an aspherical surface..

can rely. Its most important properties are the refractive index, the Abbe number (or more generally the dispersion behavior), and the wavelength-dependent transmittance behavior. Additional inevitable requirements are high optical homogeneity and low content of striae, stress birefringence, and bubbles and inclusions. Professional work with high quality materials requires precise knowledge about their properties. Hence progress in production of optical glasses and their applications is always limited by the measurement capabilities, as already Fraunhofer had realized. Since that time ever-growing quality demands in industrial and research applications have required constant improvement of measurement technology, which still continues today. Next, some of the most important achievements in measurement technology for optical glass characterization of the past two decades will be presented.

A. Refractive Index Measurement

Production control of optical glass is based on refractive index measurement of multiple monitoring samples. This requires a measurement system with a high accuracy and large throughput at low cost.

Schott uses a self-developed automated V-block measurement system, which achieves an absolute measurement accuracy (3σ) of $\pm 20 \cdot 10^{-6}$ ($\pm 10 \cdot 10^{-6}$ for dispersion) covering the visible light range and can also be extended to the range from 365 nm to 1014 nm. The relative measurement accuracy is even higher. Relative differences of samples within one V-block stack, for a set of 8 specimens cemented together in a row, can be measured up to $\pm 10 \cdot 10^{-6}$ accuracy (3σ).

Utmost precise refractive index measurement can be achieved with an automated spectral goniometer,

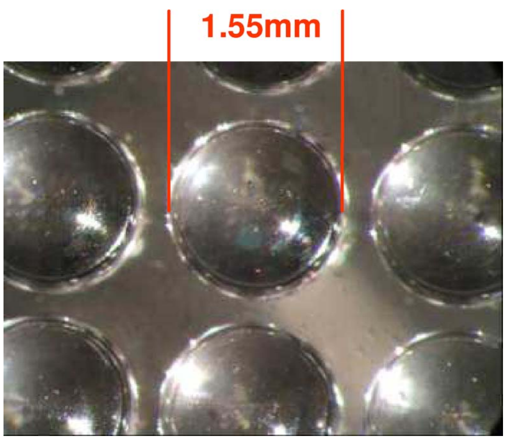


Fig. 10. (Color online) Micro-optical lens array of aspheres with 1.55 mm diameter lenses manufactured by precise pressing method.

which is called an ultraviolet to infrared refractive index measurement system (URIS). The classical method of determining the minimum deflection angle with prism-shaped samples has been optimized with a whole set of measures, the most important of which is very tight temperature homogeneity and represents the leading edge in absolute refractive index measurement (see Fig. 11).

With URIS, the refractive index of optical glasses can be measured with an absolute accuracy (3σ) of $\pm 4 \cdot 10^{-6}$ and dispersion ($n_F - n_C$) with $\pm 2 \cdot 10^{-6}$, independent of the glass type and over the complete wavelength range where glasses can transmit, which means from 185 nm to 2325 nm. The measurement can be performed at 18 to 28 °C, in air or in nitrogen. Results are given up to the sixth digit together with the Sellmeier dispersion coefficients, which allows one to calculate the refractive index and dispersion with very high accuracy in the whole spectral range from the UV to the IR.

B. Temperature Dependence Measurement of Refractive Index

Many high-end optical systems have to maintain their performance over a wide temperature range. Since the refractive index in general also changes with varying temperature, data for the temperature coefficient of refractive index are needed over a large temperature interval and a wide spectral range. Schott has developed and improved a spectral goniometer with a precision of better than $\pm 5 \cdot 10^{-7}$/K. This holds for the wavelength range 365 nm to 1014 nm. Temperature is varied in a controlled climate chamber from −100 °C up to +140 °C. The constants of the temperature coefficient dispersion formula quoted in the report allow calculating refractive index changes for given temperature intervals absolute and relative to air. The SCHOTT optical glass data sheets contain information on the temperature coefficients of refractive index for several temperature ranges and wavelengths.

Figure 12 shows the refractive index change versus temperature for several glasses at 588 nm (helium d-line). A temperature increase of 20 °C changes the refractive index of SF57 by $2.3 \cdot 10^{-4}$. The change for N-LAF2 is only a fraction of this value. N-PK51 has a negative temperature coefficient over the complete temperature range.

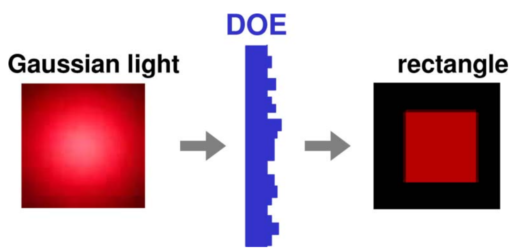


Fig. 11. (Color online) An incident Gaussian laser light is shaped into a rectangular shape by a DOE.

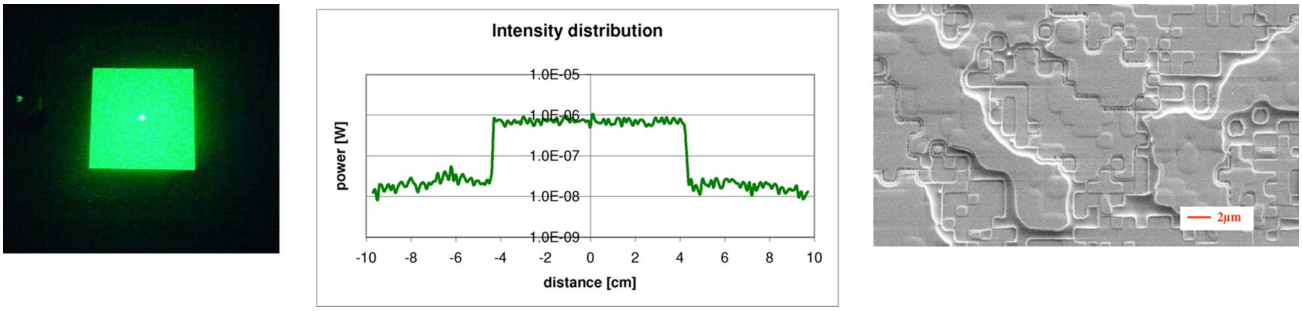


Fig. 12. (Color online) Measurement results of a glass DOE flat hat beam shaper. A photograph of the flat hat is shown (left) as well as a line cut of the intensity distribution (middle) and a scanning electron microscopy picture of the realized pressed glass structure.

C. Homogeneity Interferometry

Optical homogeneity is a key property of optical glass. For small and thin lenses the optical community has relied on its outstanding quality since the time of Otto Schott without individual inspection, which would be impossible anyway due to cost reasons. Large lenses or prisms sometimes require inspection of the homogeneity over longer spatial ranges. Especially microlithography lenses needed ultimate homogeneity proved with utmost accuracy. The rapid development of these lenses in the 1990s was enabled by the availability of a new interferometric measurement principle, the direct measuring interferometer. Since 1993 Schott has operated such a ZEISS DIRECT 100 homogeneity interferometer with an aperture of 500 mm. This device combines high spatial resolution with very high wavefront accuracy. With temperature gradients in the cavity restricted to below 0.05 °C the overall peak-to-valley accuracy is below 10 nm. For single Zernike terms such as focus, astigmatism, or spherical aberration it is half that value and even below [23].

Blanks with diameters up to 1.5 m can be measured with 500 mm subapertures. However, for such large pieces accuracy is reduced because of environmental influences such as variations in the temperature field around the blank and the interferometer and air flow in the interferometer cavity [24]. Figure 13 shows the 500 mm subaperture measurement of a 1 m sized N-BK7 blank with a thickness of 109 mm using the oil-on-plate measurement. The fine ground blank is placed between two highly polished oil-on-plates attached by means of a immersion oil film, the refractive index of which is adapted to that of the sample.

The homogeneity measurement results on the left side of Fig. 14 show the central area of the blank, measured with an aperture of 498.5 mm. The right side shows an example for the homogeneity closer to the edge with an aperture of 466.8 mm. The measured wavefront has been corrected for piston and tilt deviations and transferred to a homogeneity plot showing the refractive index variations over the measurement aperture. Both parts of the figure show homogeneity results of $2 \cdot 10^{-6}$ peak-to-valley refractive index variation on an aperture of nearly 500 mm diameter, at which the spatial resolution is approximately 1.3 mm.

D. Stress Birefringence Measurement

For small and thin glass items, which have been annealed according to common practice, stress birefringence is low enough to be negligible. But larger pieces with thickness of about 10 mm and higher can exhibit stress birefringence, which might be disturbing for high quality optics. For product quality inspection and also as feedback for the casting and annealing processes a sensitive and global measurement with high spatial resolution of stress birefringence is valuable. Especially optical glasses for microlithography again have to fulfill requirements for very low limit values.

The detailed stress measurement of a large optical component with high spatial resolution may become a time-consuming task. The higher the spatial resolution, the longer the measurement time. Most glasses react very fast to changes in the environmental temperature distribution, thus leading to variations in the stress birefringence distribution during a long time measurement. Therefore Schott uses a new automatic stress-birefringence measurement system that provides high spatial resolution together with high sensitivity and short measurement time.

Fig. 13. (Color online) Large disk of the lead flint glass type LLF1 diameter 980 mm × 210 mm, weight 0.47 tons (photo: SCHOTT).

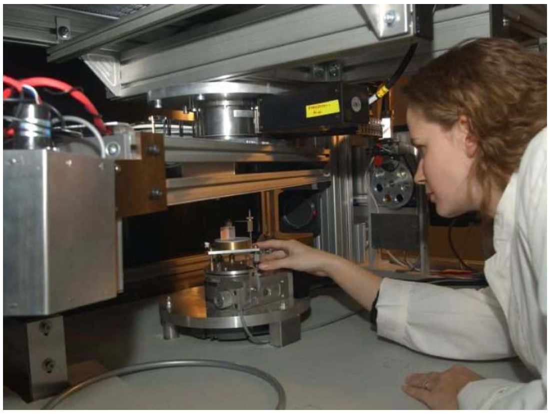


Fig. 14. (Color online) The URIS automated spectral goniometer (photo: SCHOTT).

Just recently a stress-birefringence measurement device based on the classical de Sénarmont and Friedel method became available, which enables a highly accurate and fast two-dimensional measurement of the stress birefringence of large samples up to 300 mm diameter. The system was adapted to the special requirements of Schott. Its spatial resolution lies in the 1 mm range, with the noise level below 0.5 nm optical path difference and the measurement accuracy at ± 1 nm. Figure 15 shows the result of a 300 mm diameter glass blank.

E. Striae Measurement

Striae are spatially short-ranged refractive index variations in optical glass caused by various factors. Traditionally they are inspected using the shadowgraph method. A glass sample is placed between a divergent spot such as a Hg arc lamp and a screen (see Fig. 13). The contrast of the striae is compared to reference samples with different striae grades. This method is very sensitive, but a real physical quantification of the results in terms of wavefront distortion was not possible up to now. Interferometric measurements can be done in principle since with the direct measuring interferometry a method with sufficient resolution and sensitivity is available. But the very high spatial frequency, the strong directional dependence of striae, and the sample preparation requirements make it a difficult task that requires effort. Therefore the much simpler shadowgraph method is still the method of choice for striae measurement.

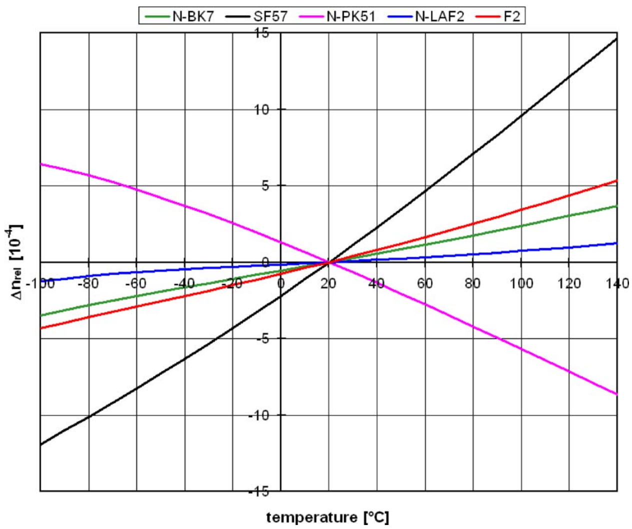


Fig. 15. (Color online) Change of the refractive index at the helium d-line at 588 nm versus temperature of some different glass types. The refractive index is relative to air, and catalog values are relative to 20°C.

In order to get rid of the old striae classification types A to D according to the expired military standard MIL-G-174B, Schott introduced levels of wavefront distortion that correspond to the A—D grades on the basis of measurements made on reference samples. The A, B, C, and D grades were found to correspond to four degrees of wavefront distortion: about 10, 15, 30, and 60 nm.

Just recently an important achievement was made on the way to a physical measurement of striae in wavefront distortion. The shadowgraph setup was equipped with a CCD camera taking pictures of the screen image and assigning a contrast value to each stria. The contrast values could be reproduced within about 5%. Glass plates with artificial striae produced by coatings with different thicknesses were used as reference to investigate the influence of different combinations of phase shift and stria width. It could be shown that there is no unambiguous relation between the contrast of a stria and its phase shift. The same contrast could be found for artificial striae with different combinations of phase shifts and widths. A deeper analysis of simulated diffraction patterns of model striae showed a dependence of the first minimum of the Fourier power spectrum with the stria phase shift and width (see Figs. 14 and 15). The combination of Fourier analysis of striae patterns and contrast measurement can remove the ambiguity and obtain well-defined wavefront distortion results [25].

The measurement results are satisfactorily reproducible and can be transferred to volume striae. The

Fig. 16. (Color online) Homogeneity measurement of a 1 m diameter glass blank using a ZEISS DIRECT 100 interferometer at 500 nm aperture [25].

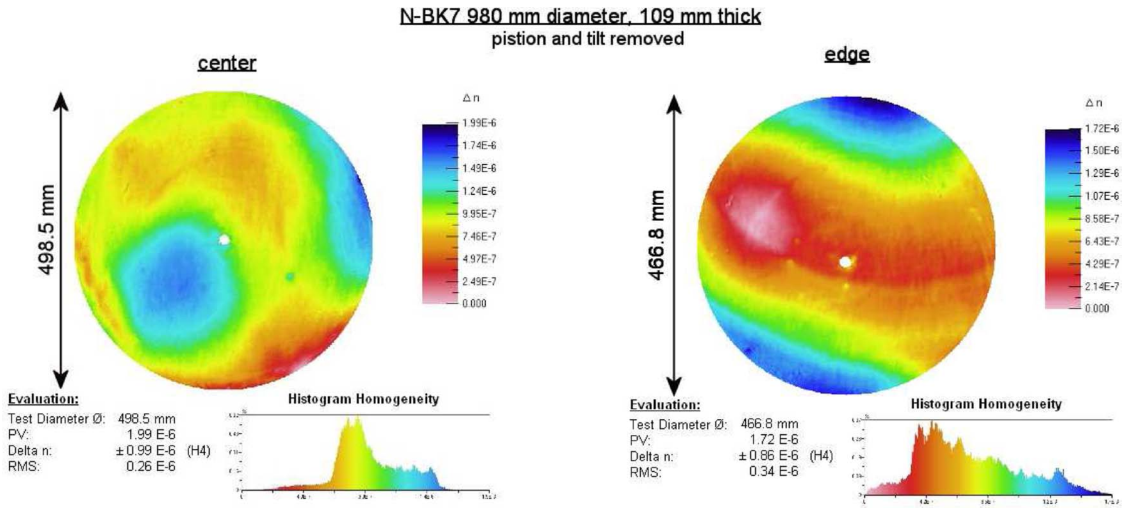


Fig. 17. (Color online) Homogeneity measurement results of a 1 m diameter N-BK7 glass blank [25].

sharp drop in striae visibility with slight turning angles between the glass sample and the observation direction reduces them to two-dimensional effects in practice.

Since many years attempts have been made to introduce a striae measurement method, which is not only simple and highly sensitive but also reproducible and directly related to the world of optics design. For more than 20 years stria inspection standard proposals failed because both preconditions were not fulfilled [26]. Therefore we consider the findings as a breakthrough on the way to get quantitative results from a shadowgraph setup, which an optical engineer can take into account in designing a lens system.

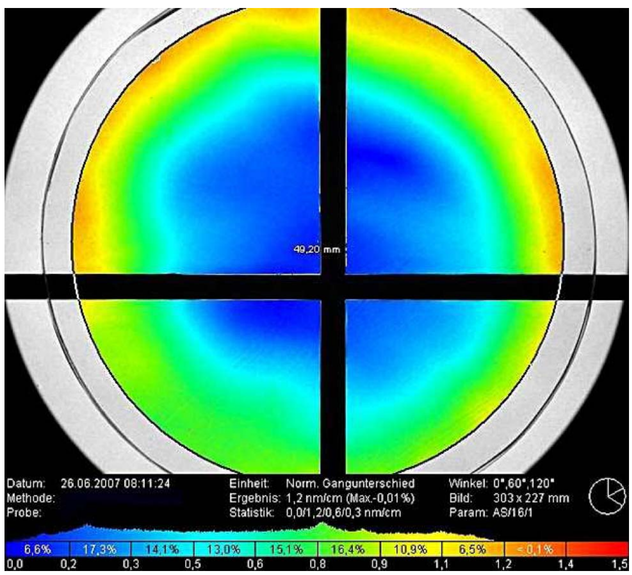


Fig. 18. (Color online) Stress birefriengence measurement of a glass blank with 270 nm diameter (measured: 238 mm) and 49 mm thickness. The darl cross comes from the disk support. The color coded scale spans from 0 (dark blue) to 1.5 nm/cm (dark red) [25].

14. Zero-Expansion Glass Ceramic ZERODUR

The demand for ever larger diameters started as early as when Galileo built his first telescopes. Refracting telescopes reached their limit of 1 m lens size with the Yerkes telescope by the end of the 19th century. Mirror telescopes took over and pushed the limit to 5 m (Mt. Palomar) by use of low-expansion borosilicate glass. For the next step in improving telescopes the influence of environmental temperature gradients had to be minimized further. That was the time when ultralow expansion glass ceramics entered the scene.

Since its development in 1968 the ultralow expansion glass ceramic ZERODUR [12] has been steadily improved further. This relates not to its composition but to the melting and ceramization processes as well as shaping via precision grinding, metrology, and knowledge about the material properties.

Since the production of the first 4 m mirror blank for the Calar Alto Observatory in Spain ZERODUR has been used successfully in a wide range of highly challenging projects such as the 4 m telescopes ESO-NTT, TNG Padua, AEOS Maui, VISTA, the 8 m telescopes ESO-VLT, the 10 m telescopes KECK I and II, GRANTECAN, and the x-ray satellite telescopes ROSAT and CHANDRA. With monolithic mirror telescopes Schott demonstrated their capability to achieve large dimensions and with the segmented telescopes the capability to achieve long-term reproducibility of high quality elements in the 2 m diameter range.

This reproducibility is a special requirement for the two future extremely large telescope projects, the 42 m diameter mirror European Extremely Large Telescope (E-ELT) of ESO and the American Thirty Meter Telescope (TMT) telescope. Both telescopes need their hexagonal segments of about 1.4 m width to be produced over several years with constant high quality in order not to destroy serial polishing as a result of the need for adjustments to varying quality of the segments. Both projects also have in common very tight specification

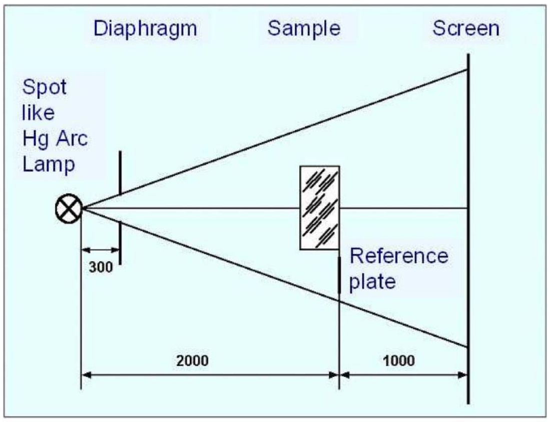


Fig. 19. (Color online) Shadowgraph setup for stria inspection. Right: application in practice. The main problem is to calibrate its results in relation to optics design via the wavefront distortion and structural width (photo: SCHOTT) [32].

requirements regarding the thermal expansion behavior in the planned observatory environment and on the radial and axial homogeneity of the mirror material.

ZERODUR is not only used in major ground-based telescopes but has also been used in satellites for more than 30 years. Some examples are ROSAT, CHANDRA, Hipparcos, the Hubble telescope secondary mirror, the Meteosat Second Generation (MSG) satellites, and the SPOT Satellites. A series of 30 space applications together represent more than 100 years of operation lifetime in orbit, illustrating the significant space heritage of ZERODUR [27].

A. Thermal Expansion Coefficient of ZERODUR

The coefficient of thermal expansion (CTE) used to characterize ZERODUR is defined as the static thermal expansion difference between 0 °C and 50 °C and is measured using 100 mm samples in a push-rod dilatometer. The absolute accuracy up to now is ±10 parts in 10^9(ppb)/K, and the reproducibility is ±5 ppb/K (95% confidence level) [28,29]. For the characterization of the CTE of a large mirror blank, typically 6 to 18 CTE samples are taken directly near the final blank geometry at the outer circumferential area. From the results, the mean CTE and the CTE homogeneity (global peak to valley and axial gradient) can be evaluated. The axial gradient is defined as the difference between the mean CTE of the back and the front surface of the material.

In recent years the dilatometer has been improved with an interferometric measurement system [30,31]. The absolute accuracy of the improved dilatometer for the CTE (0 °C, 50 °C) measurement is now ±6.2 ppb/K, and the reproducibility is ±1.2 ppb/K (95% confidence level). Because the accuracy of homogeneity measurement is given only by reproducibility, the CTE homogeneity of a ZERODUR mirror blank can be measured to ±1.2 ppb/K. The axial gradient can be evaluated to ±0.9 ppb/K [32]. Extensive investigations have been completed using the improved dilatometer setup to get a deeper understanding of the CTE homogeneity of ZERODUR within single blanks and the production format of multiple ELT segment thickness.

B. Homogeneity of the Thermal Expansion Coefficient of ZERODUR

Figure 19 shows the results of a detailed homogeneity measurement on a single 1.5 m diameter 345 mm thick blank of ZERODUR in 2008. The deviations of the single measurements of 90 samples (evenly distributed over the complete diameter) from the mean value of the blank are displayed in a two-dimensional plot. The peak-to-valley CTE homogeneity of the blank is <4 ppb/K, and the axial gradient is 0.5 ppb/K on 50 mm thickness. This blank has been taken from the standard production and not been specifically selected for this evaluation.

A detailed investigation of an additional single boule yielding several 1.5 m blanks, which was done according to a sampling plan proposed for ELT production, showed a total CTE homogeneity of 5.1 ppm/K [32]. The axial gradients of blanks cut from the boule in the majority are below 1 ppb/K. The results show no systematic radial or axial variations of the CTE within the complete boule with

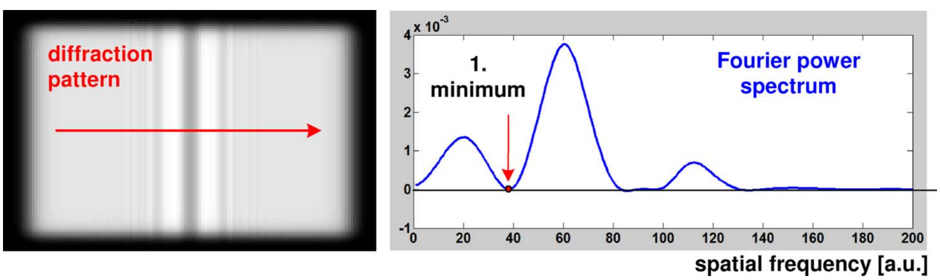


Fig. 20. (Color online) Fourier spectrum of a section through the diffraction pattern of a slit width phase step [26].

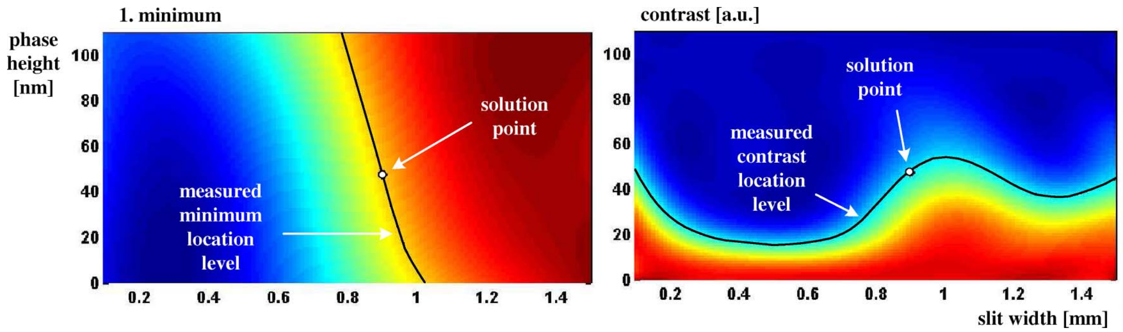
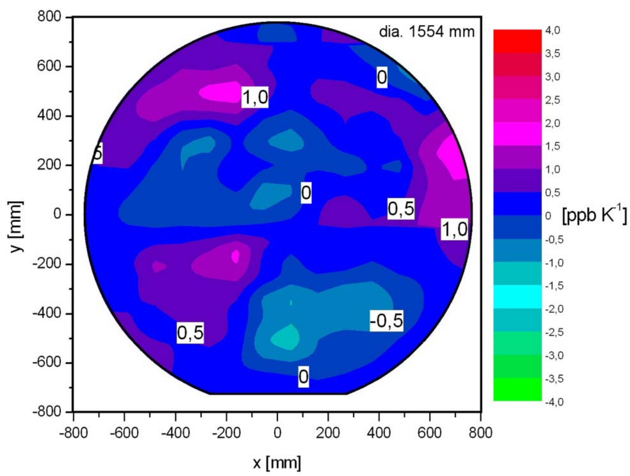


Fig. 21. (Color online) Reconstruction of the phase height and the slit width from measured data of the contrast and the position of the first minimum of the Fourier spectrum [26].

respect to the measurement reproducibility of 1.2 ppb/K.

The CTE homogeneity statistics of more than 30 blanks cut from material produced in 2008 has been evaluated and compared with the results from the Keck and GTC projects, which were published in 2005 [33]. The maximum variation (peak to valley) observed within the more than 30 blanks from 2008 is smaller than 10 ppb/K. The mean value over all homogeneity measurements is 4 ppb/K. The new evaluation shows an improvement by a factor of 2 in terms of CTE homogeneity versus the ZERODUR delivered for GTC and Keck [32]. This obviously comes from better measurement accuracy rather than from the material itself, which was already highly homogeneous then.

Figure 20 shows the frequency distribution of the absolute axial CTE gradient of the blanks in comparison with the results for the Keck and GTC projects. The maximum axial gradient observed is equal to or smaller than 2 ppb/K. The mean axial CTE gradient over all measurements was 2.8 ppb/K for the Keck project and 1.2 ppb/K for GTC. The mean axial CTE gradient of the new evaluation is 0.6 ppb/K, showing again an improvement by a factor of 2.



[ppb K-1]	blank 2008
Mean CTE (0°C, 50°C)	39.9
CTE homogeneity (pv)	3.8
Mean axial CTE gradient on 50 mm thickness	0.5

Fig. 22. (Color online) CTE homogeneity results of a single blank from 2008 [34].

The results shown here are a record of the impressive long-term reproducibility of the CTE homogeneity of ZERODUR over a production time of 22 years, which lies between the production of the first Keck segment in 1986 and the results of the boules produced in 2008. The excellent CTE homogeneity exceeds the specifications that are the current baselines for the ELT projects.

C. Modeling of the Thermal Expansion Coefficient of ZERODUR

The thermal expansion of ZERODUR is not only a function of temperature but also a function of time, due to the so-called structural relaxation that is typical for all glass ceramics [34,35]. The application temperature range of the upcoming ELT projects varies depending on the possible construction site between −10 °C and +25 °C or between −13 °C and +27 °C. Typical temperature change rates during the night are in the range between 0.1 °C/h and 0.3 °C/h. Such temperature rates are much smaller than the typical possible laboratory measurement rate described above.

Schott developed a model to describe the structural relaxation behavior of ZERODUR. With a combination of global ZERODUR material parameters and such material parameters that have to be generated for the individual batches using a special measurement procedure, it is possible to precisely predict the thermal expansion behavior of the individual material at arbitrary application temperature profiles $T(t)$.

Figure 21 shows the modeled thermal expansion of two different ZERODUR samples under the night- and daytime temperature profile as measured for the Subaru telescope on Mauna Kea [36]. The sample 2 has a higher CTE at application temperature conditions compared to sample 1, despite the fact that its CTE (0 °C, 50 °C) value is closer to zero compared to that of sample 1. With this model it is possible to adjust Zerodur for very critical applications, taking into account the specified temperature interval and change rates for lowest possible expansion.

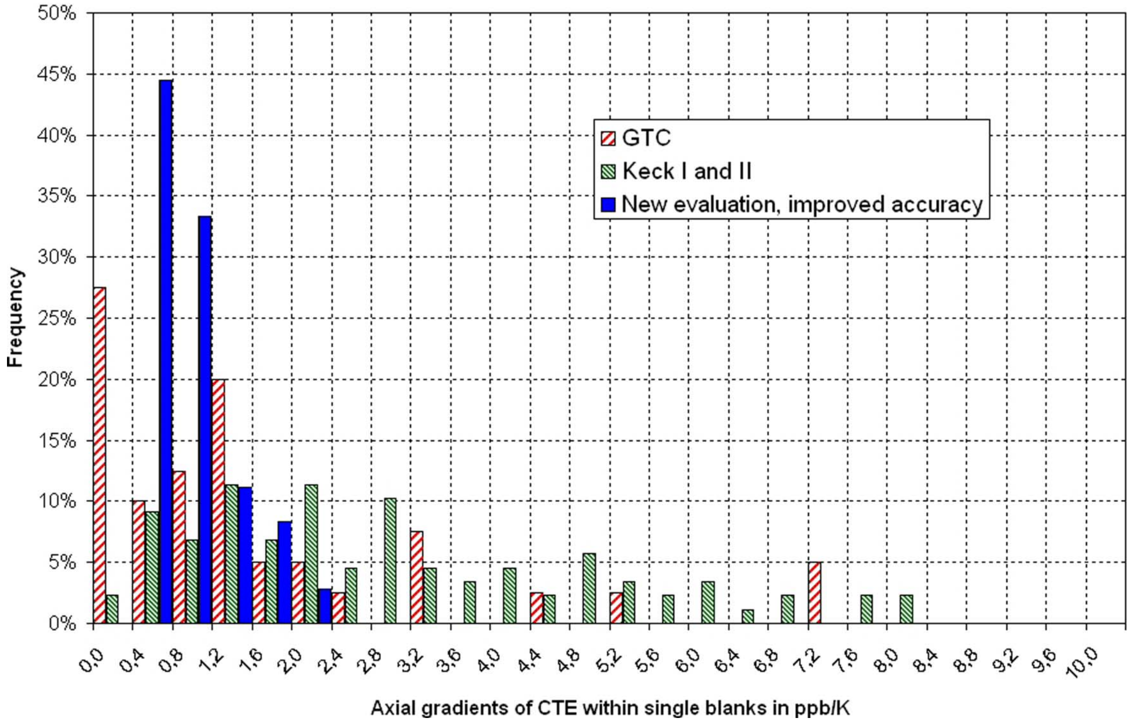


Fig. 23. (Color online) Frequency distribution of the axial CTE gradient of more than 30 blanks produced in 2008 compared to the results achieved during the Keck and GRANTECAN (GTC) projects [34].

In ELT specifications the mean CTE is specified with respect to the application temperature range and temperature rates instead of just defining the CTE (0 °C, 50 °C). In this case the model developed by Schott allows the exact tailoring of ZERODUR CTE to the ELT application temperature conditions on the mountain top.

D. Improved Processing: Lightweighting of ZERODUR

In the past ZERODUR mirror substrates for space applications have been reduced in weight by 40% to 75% by grinding a hole pattern from the backside into the massive part with computed numerically controlled machines. The rib thickness between the holes was mostly designed to values of about 5 to 8 mm for a typical rib height of about 100 to 200 mm. With the conventional process thinner ribs were not possible because of the high risk of breakage during grinding especially for high ribs. Recent process developments at Schott led to the capability to grind 2 mm ribs with 190 mm height (see Fig. 19). The final faceplate thickness after grinding is typically in the range of 10 to 20 mm. This can be optimized by grinding of a curved bottom by approximation with small steps, which is also possible now at Schott. In general the design for the lightweight structure is provided by the customer, as the mirror is an integral part of the telescope design. The designed thickness of the faceplate mostly depends on the print-through or quilting effect during the polishing process. The thinner the faceplate and the larger the holes, the higher the risk of faceplate deformation during polishing. Sometimes ion-beam-polishing methods are applied for final surface fine correction.

An additional etching process, often applied for ZERODUR components in space applications, reduces surface stress induced by grinding and increases the bending strength significantly. In addition it is also possible to extend the acid etching process for a substantial additional material removal, ending up with rib thicknesses even below 1 mm; see Fig. 19 [37] .

A series of breakage tests with different surface conditions (coarse and fine ground as well as etched) has been performed in order to demonstrate that

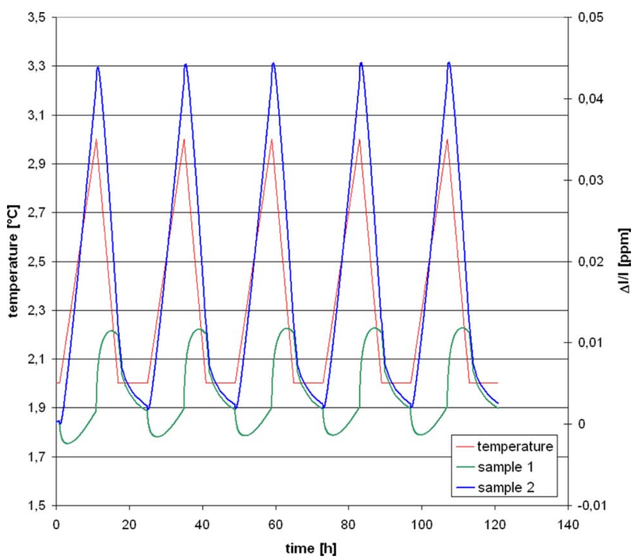


Fig. 24. (Color online) Modeling the thermal expansion behavior of two different ZERODUR® samples for a temperature variation of 1˚C from 2˚C at 12 hours per night [34].

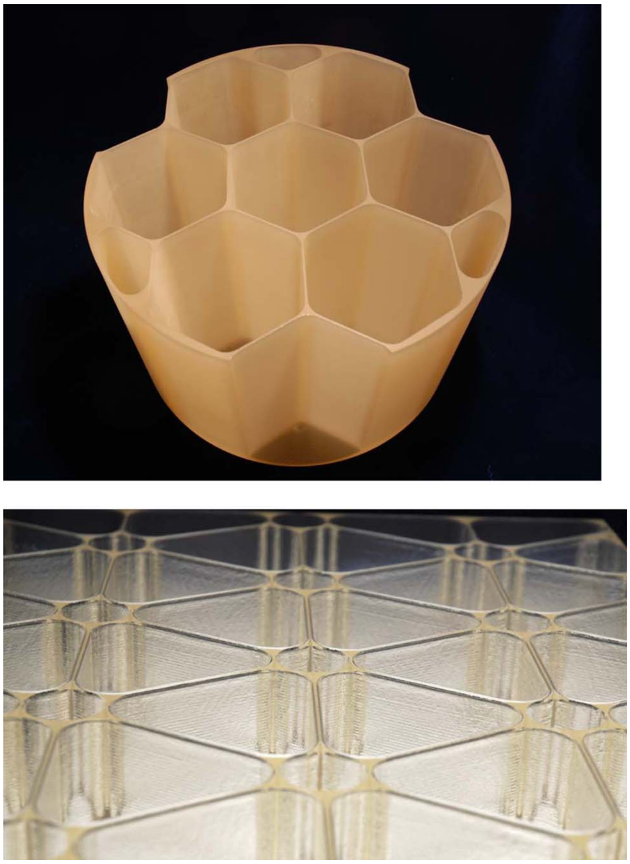


Fig. 25. (Color online) Demonstration lightweight structure with 2 mm rib thickness 190 mm high (left) Etched structure with 0.65 mm rib thickness (right) [38].

ZERODUR is strong enough to survive launch vibrations. This strength has been verified with original sized sample structures in vibration tests [38].

The largest lightweighted astronomy mirror produced up to now from ZERODUR is the 2.7 m primary mirror of the airplane-based SOFIA telescope, with the lightweighting process performed at SAGEM (France). With existing CNC machinery the present manufacturing limit at SCHOTT would be a 4 m class lightweighted mirror blank.

15. Conclusion

Optical glass and glass ceramics have enabled developments in research, technology and medicine, which can hardly be overestimated. There has been steady progress in developing new glass types, their production processes, and property characterization especially in the past two decades, which is still going on and will go on in the future since there will come even more demanding applications that will challenge the materials and all the processes around them.

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