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Views

Optical glass: past and future of a key enabling material

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Glass has been in use for more than 5000 years. Within the past 130 years it became the subject of scientific advancement towards a material of precisely predictable and reproducible properties. As such, it was a crucial element in the technical revolutions of the 19th and 20th centuries. However, glass development did not stop. Today, environmental and not least economical aspects play an important role in the dramatic change of glass materials and their availability. Almost 90% of glass types have vanished from catalogs in recent decades, whereas new materials are being rapidly developed.

1. Technological vs. economic value

It was a long and tedious path to precision optics. The immeasurable and still ongoing technological revolution enabled by precision optics started when optical glass became a technical material, which Otto Schott achieved approximately 125 years ago in Jena, Germany, in close cooperation with Ernst Abbe and Carl Zeiss. The progress made was strongly related to achievements in optical glass manufacturing such as improvement of glass quality or the introduction of new glass types beyond the few existing crown and flint glasses with markedly different dispersion properties [1].

The subsequent developments of precision optics after the improvements in glass quality demonstrated how large the demand had been. For example, the availability of high-performance microscopes boosted medical research. They strongly supported the successful fight against infection diseases, which extended average human lifetime by approximately 20 additional years.

However, the strong demand for optical systems does not reflect immediately in equally strong demand for optical glass material. Glass has a typical share of 1–2% or less of the total value of optical systems. Schott has not become a large company on the sales of optical glass but due to sales of spin-off products such as gas lamp cylinders. The borosilicate glass used in these cylinders was invented in search of new optical glass types. From a purely economic view the sale of optical glass is a very small business compared with other material supply business or with glass sales for consumer applications. However, optical glass is literally at the core of all optical systems and all technology relying on them would be useless without glass.

2. Making glass is meeting extreme technical requirements

Since the first lithium glass that Otto Schott created in 1879 many glass types have been developed (Figure 1). On introducing additional chemical elements the range of index of refraction and dispersion combinations has been extended largely. Fluoride and fluorophosphates glasses, borosilicate, barium- and lanthanum-containing glass types add low dispersion variants for given refractive index levels [2].

The new materials pushed an enormous progress in glass processing technology: some glass types required new melting processes, others are chemically so aggressive that they would destroy the traditionally used clay pots. Many of them have a high tendency to crystallization. With the traditional melting and casting method they would not become glasses at all.

Changing to a continuous melting process, which is called tank melting, resulted in significant cost reduction. One reason for this being the much better yield of good glass from the same amount of raw material and the other being the much higher energy efficiency.

The continuous rise in requirements on the performance of optical systems also had consequences on optical glasses. Diffraction-limited systems being exceptional in the past have now become the rule even in consumer optics. This leads to extreme specifications for the glass.

Although it is not very difficult to fulfill such requirements with glass parts as small as several millimeters in diameter and thickness, challenges increase with large components overproportionally. Optical homogeneity of better than 1×10^{-6} across 5 mm diameter should be self-evident for a piece of glass being called optical glass. Across 30 mm diameter this is no longer a given in any case, for 200 mm it is an art, and beyond 500 mm it is an outstanding achievement. In particular, the application of optical glass in microlithography posed extreme requirements to all specification characteristics. Even the narrowest catalog tolerances were no longer sufficient and had to be surpassed considerably for all characteristics at the same time and reliably for a large series of large discs (Figure 2). The necessary developments in melting technology, measurement methods and quality assurance have been costly but led to sustained success. Optical homogeneity levels well below 1×10^{-6} could

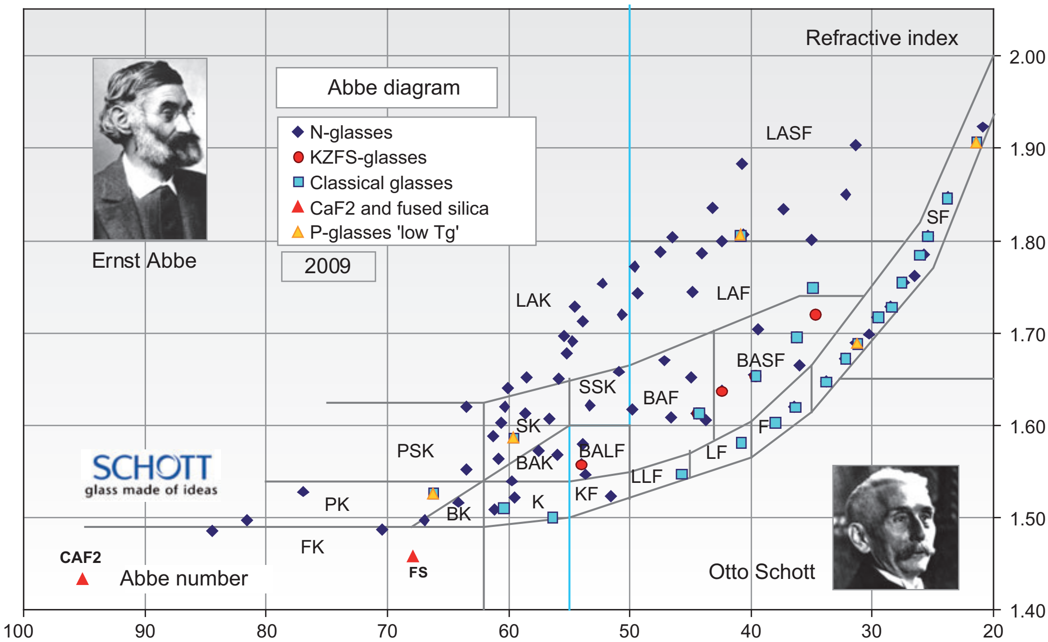

Figure 1 The Abbe diagram provides an overview for the portfolio of existing glass types plotting their optical positions within the refractive index and dispersion grid. The dispersion is characterized with the Abbe number, which is given traditionally in reverse order as dispersion rises with decreasing Abbe number.

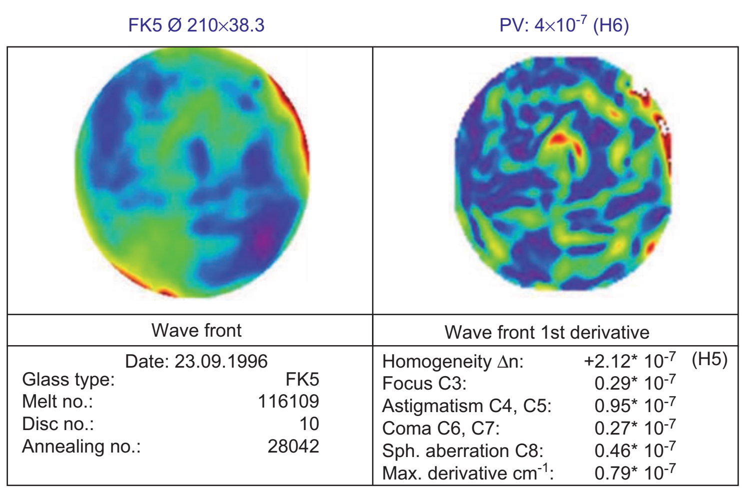

Figure 2 Optical glass blanks for use as lenses in microlithography are specified with extremely narrow tolerances. With simultaneous development of melting and measurement technologies it became possible to deliver thousands of large blanks with extreme homogeneity.

be reached for diameters larger than 200 mm and thickness of 40 mm not only for single pieces but for thousands of them [3].

3. Some recent developments

Approximately 20 years ago new developments in optical glass arose from Asia. First, they were underestimated by the Western world probably because their main use was for consumer optics, a field of optics that has largely moved from Europe and North America to Asia. The company Hoya of Japan introduced a process for cost-effective series production of aspherical lenses, the so-called precision molding. From preforms, which already provide highly smooth surfaces, they press finished lenses in precision molds. The lenses only have to be centered and coated to be ready for mounting. The process is performed at the lowest possible temperature just enabling plastic deformation. This method preserves surface quality mostly and avoids early wear of the pressing tools. The main drawback is its limitation to small lens diameters and thicknesses. Larger lenses require long cooling times to achieve the necessary high homogeneity and low stress birefringence. Production cycles would be too long to be economic. As the precision molds used are very expensive the method is only economic for large series, which are typical of consumer optics.

The second trend relates to environment-friendly glass compositions. The portfolios of all glass manufacturers currently comprise large numbers of lead- and arsenic-free glass types. The benefit for the environment will be very moderate considering the comparatively small amount of optical glass produced worldwide and the extremely low risk that any of its constituents may become bioavailable. Nevertheless, it is understandable that producers of consumer optics avoid lead or arsenic if they want to maintain their environmental-friendly image. Changing a large part of consumer optics to ecoglass types did not lead to performance impairment. A smaller market, however, suffers from the considerably lower transmission of the lead-free glass types in the blue violet spectral range, this is digital projection. A true color projection needs three color channels with equal intensity. The blue channel usually is the weakest already coming from the lamp. This and additional losses in the glass must be compensated by damping the other two channels leading to difficult heat management in the projector and high energy waste. In industrial optics, a lot of essential applications depend on high blue-violet transmission and those applications become impossible with lead- and arsenic-free glass types.

4. A 90% change in the glass type availability

The 1990s saw dramatic changes in the glass programs of all manufacturers. Although having grown steadily since the time of Otto Schott up to a peak of 273 glass types in 1967, the Schott glass portfolio consolidated in subsequent years until a sharp drop occurred close to the turn of the millennium (Figure 3). Two trends met at that time: the demand for the ecoglass types and the need to abandon long-term uneconomic glass types. This led to the loss of 90% of the classical glass types of the Schott catalog of 1992 with respect to the 1999 edition. Only 20 glass types remained and 66 new ones entered as lead- and arsenic-free replacement glass types on important positions in the Abbe diagram. This was a huge effort for Schott and for all affected industrial optics companies. Other Western glass manufacturers have not joined the effort and have abandoned the market completely or shrank to insignificance.

Since 2000, Schott introduced more than 30 new glass types, 15 of them in the years from 2009 to 2011. The level now reached at slightly above 100 seems to be sufficient for most of today's optical systems and restricted enough to be provided by a single glass manufacturer sustainably [4].

5. Progressive and adverse trends

After the remarkable changes in the product variety, a number of new trends and some more traditional demands became apparent:

- High refractive index glass types for short system length and for lower spherical aberration.
- Low dispersion glass types for correction of secondary color aberrations.
- Quality variants of glass types with high transmission in the blue-violet light.
- Glass types for precision molding with lowest possible transformation temperature and low interaction with the mold material.
- Lead- and arsenic-free glass types.

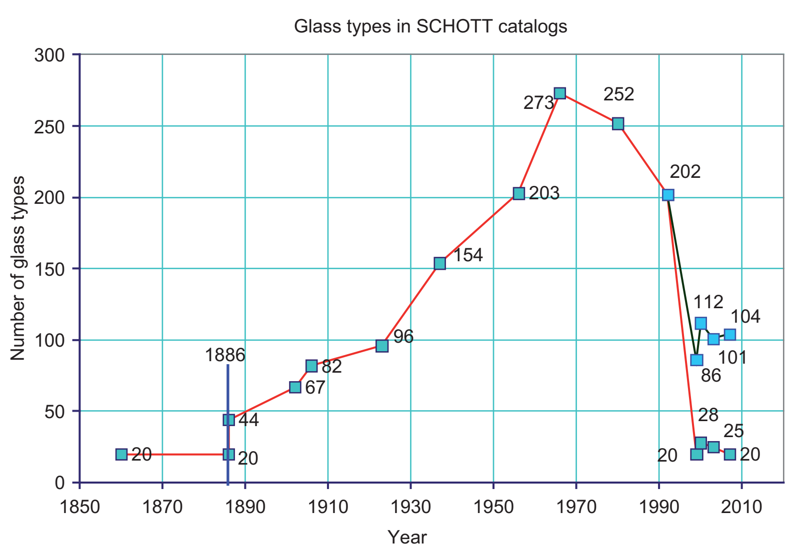

Figure 3 The total number of optical glass types in the Schott catalog editions shows a dramatic change in recent history. The drop from 1992 to 1998 was due to the necessity to abandon uneconomic glass types with very low market demand and to change the glass portfolio to lead- and arsenic-free glass types. (Red line: classical glass types, black line: total number of glass types.)

Considering the strongly grown number of digital cameras and cameras in mobile phones one might think that the need for optical glass grows accordingly. This is not the case due to several reasons.

- Because of its lower density and price plastic optics (or polymer optics) replace glass. This has reached a share of more than 90% with the use for spectacles.
- Optical elements become miniaturized, reducing the material needed.
- Different functions distributed on several elements are now combined in one element.
- Aspherical lenses replace two or more spherical lenses.
- Smaller near-net shape glass preforms (precision gobs or rods for precision molding) give higher yield.
- Electronics replace optical systems as view finders, displays instead of pentaprisms with SLR cameras.

Additionally for European/US glass manufacturers.

- Large glass volumes demand for consumer optics went to Asia.
- European and US industrial optics manufacturers purchase material from Asia for lower prices.

These reasons might lead to endangering the existence of European and US American optical glass companies (Figure 4). Smaller demand leads to smaller production lots and thus higher costs. A growing number of optical glass types might fall below technical or economical limits and hence be lost from the glass portfolio. Only a minimum profit enables developments. Reduced margins lead to fewer innovations. This also holds for customer service such as provision of special quality grades, data and information, technical consulting, standardization work and lobbying activities. Customers expect all this from glass manufacturers but the financial requirements of such services are easily overlooked. Purchasing only from the cheapest source may turn out as extremely expensive in the long term.

The change in the glass supply landscape (see Figure 4) leaves SCHOTT AG as the sole manufacturer of optical glasses in the Western world. This might be already seen as a warning sign for a critical change in the availability of optical glasses.

Figure 4 The present-day world map of optical glass manufacturers shows a concentration in Asia with only a small portion left in Europe and in the USA.

6. RoHS: threats beyond the ban of lead and arsenic

Since 2003, another adverse trend appeared that might become a serious threat to total optical industry. In that year, the European Commission released directives to increase the share of recycling of electric and electronic waste. To support this goal the content of several hazardous substances was limited to 0.1%, among which is lead, and to 0.01% for cadmium. As optical and filter glasses usually are components of electronic devices, these materials also became subject to the directive RoHS (Restriction of certain Hazardous Substances 2002/95/EC) [5].

Together with the German Industrial Federation Spectaris representing many companies from optics, precision mechanics and medicine and Carl Zeiss AG and with support from international optical companies Schott AG succeeded in obtaining an exemption for optical and filter glasses in 2005. These glass types are essential for many highly important applications in medicine, safety, environmental surveillance and general research and development. The loss of these applications would be in vast disproportion to any environmental benefit, which is so minute that it is difficult to prove its existence at all.

The company consulting the European Union (EU) in preparation of the exemption decision agreed with this view. Unfortunately, the EU granted the exemption only for a period of 4 years as a routine measure to maintain innovation pressure on industry. In September 2010, the exemption was extended for another 4 years and by July 1, 2011 it was extended again on the occasion of the release of the revised RoHS (directive 2011/65/EU, the so-called RoHS recast) to July 20, 2016.

From today’s point of view this might seem to be comfortably far away in the future. However, this may turn out to be short-sighted. Optical designs of high-performance systems need long-term reliability in optical glass availability. From the start of a new design based on existing glass types usually 2 years and more pass before the market entry of the new optical system. Even after 5–10 years market presence spare parts have to be guaranteed, for special systems even up to 30 years. The expiration and extension procedures established by the revised RoHS do not help to remove uncertainties from the exemption periods. The remaining time for glass types will shrink to 6 months before the expiry date, and in special cases even down to 3 months. No one can use a material for a long-term design if there is a risk that it will be prohibited before the product is launched.

There is another risk for the long-term availability of optical materials. More chemical elements might be added to the prohibition list. In the revision phase of RoHS the elements arsenic and antimony were under consideration. Both elements are in use with optical glass with contents fairly below 1%, but in many cases above the usually set limit value of 0.1%. Their purpose is to prevent high levels of tiny bubbles in glass. This refining effect comes from their change in valence bonds from three at high temperature to five at low temperature, which enables them to integrate gas atoms into the atomic network of glass. Even though arsenic had already been removed from many glass compositions it is still necessary for special applications, where classical glasses cannot be replaced because of their unique combination of high refractive index and high blue-violet transmission. This combination requires the presence of lead and arsenic together. Antimony had been the replacement element for arsenic in many glass types during the redevelopment of optical glasses in the 1990s. There is no replacement for antimony, so that banning this element would lead to the loss of many glass types (Figure 5), even though some might be rescued by reducing the content below 0.1%.

The directive RoHS asks for regular revision of the substances prohibition list if additional substances should be added. Beyond arsenic and antimony, boron, selenium, cobalt and nickel had been in discussion already. Boron would lead to additional losses of important glass types. With selenium, cobalt and nickel being prohibited, not a single colored filter glass would exist any longer.

Generally, heavy metals are in the focus of observation. As there is a considerable number of heavy metal elements in use with optical glasses, filter glasses, special optical glasses and optical glass ceramic, there is a high probability that such glass types might become subject to future prohibitions.

For each element added to the prohibition list there would be the need for an exemption application. Case-by-case the necessity of each element would have to be proven on the basis of objective retrievable data considering possible alternatives, the whole product lifetime and possibly exchange plans. At best, one could get 5 years exemption with the need to apply for an extension latest 18 months and granting decision 6 months before expiry. The resulting research and administration effort would mean not only the complete loss of profit for many glass types, it would even be higher than the total turnover for many glass types and hence would lead to the complete loss of many glass types. With such an unreliable material basis precision optics would be in question as a whole. Knowing about the key enabling character of precision optics for many other far bigger technology branches this could lead to widespread stagnation and regress.

7. Exempt optical glasses from RoHS

By contrast, any environmental benefit is doubtful. The reduction potential for each possibly declared hazardous substance in optical glass is below one part per million in most cases, even much lower than that in relation to the total amount of electric and electronic waste. Here is one example. The total amount of cadmium used in filter glass was 0.3 tons worldwide in 2007, the amount of electrowaste just in Europe was approximately 10 million tons. This content is completely negligible even if cadmium in electrowaste were to be bioavailable, i.e., could enter biological organisms. However, it is like all other ingredients firmly bound in the atomic network of the glass. There are no mechanisms allowing elements to leave the bulk glass in considerable amounts, not even in waste incineration plants. In fact, one of the best ways to take elements out of bioavailability is to melt them into glass.

If environmental valuation is not restricted to the presence or absence of hazardous substances but widened to take

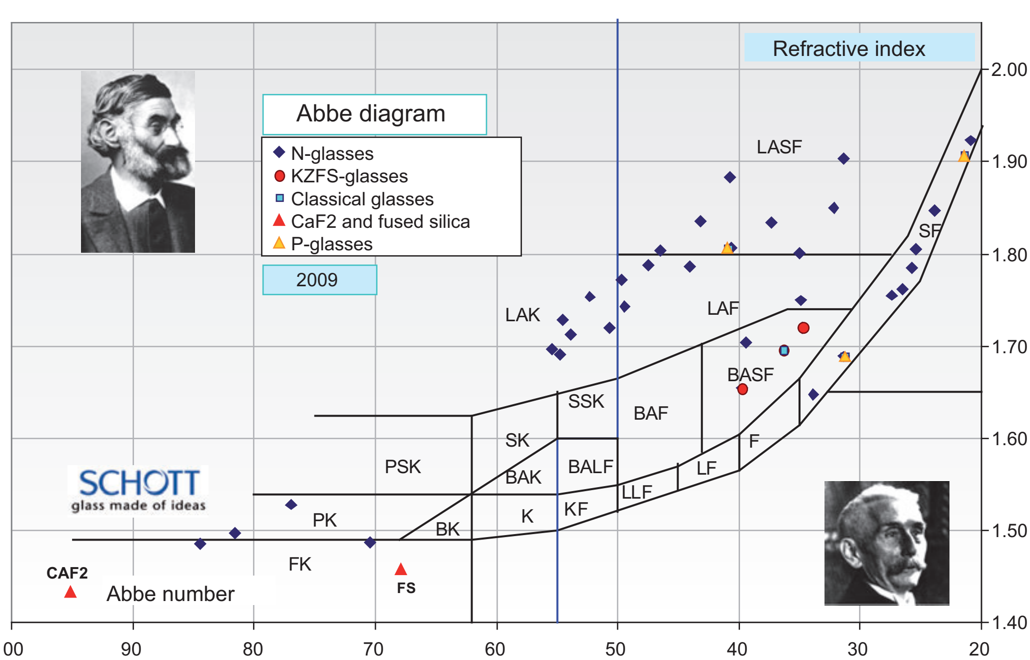

Figure 5 If the EU directive RoHS were to restrict the use of arsenic and antimony to contents below 0.1% most optical glass types would be lost. There would be wide regions where no glasses would be left at all. Such a restriction would have severe implications for precision optics and its downstream applications.

energy consumption into account the lead-free glasses lose their benefits, if there were any at all considering the arguments above. The more lead replaced in the glass composition the higher the differences in processing temperatures relevant for melting, pressing and fine annealing. Usually, lead-free glass types require much more energy not only in the melting process but also in the subsequent reheat press processes.

The EU as well as the German government have recognized their large heritage in optics and photonics with many companies and institutions forming a broad basis of leading edge capabilities. They have realized the tremendous leverage effect of photonics on other technologies of even much higher economic importance. Therefore, they have committed themselves to support research and development with a high level of funding within the next 10 years. However, it is not only important to acquire new capabilities but also to maintain the high standard, which has been achieved already and that is needed for many high-ranked EU objectives such as technical competitiveness, safety, health, climate and environment protection. The disproportion between the negative consequences of prohibiting chemical elements for use with optical materials and the extremely minute benefit for the environment is so extraordinary large that sometimes it is forgotten that the regulations are ranked as laws enforced with the possibility of personal punishment.

For this reason, the next target will be to have optical materials taken out of the RoHS scope in total. High-quality optical glass, filter glass and optical glass ceramics are key enabling materials of the present and the future. Their availability is not self-evident. The users should support the supplier, who takes the effort to get the removal done by the EU, by contributing additional cases to the collection of applications, where possibly endangered glass types are indispensable, and by open confession to this need.

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Peter Hartmann serves as member of the Board of Directors of SPIE from 2011–2013.