Optical glass:
an interplay of challenges and success

For several hundred years, there has been an impressive interplay between optical design and optical glass development. Step by step, imaging by lenses in microscopes or other optical instruments has almost reached perfection. Simultaneously, optical technologies have broadened their application field by entering, *e.g.*, the area of telecommunication and being even the driver of novel technologies like augmented reality. Remarkably, even with the latter dramatic change in optics, there has been a red thread concerning the desired material properties so far. However, with today´s nanotechnologies, also completely new approaches may contribute to the field of optical materials in future. Who knows?

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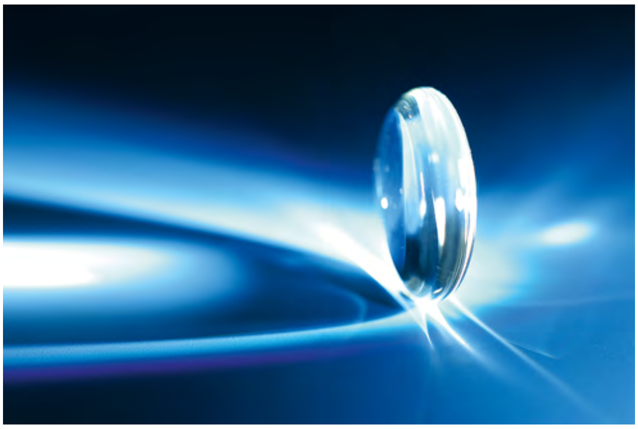

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Introduction to Optical Glasses

Optical glass has a long history and has been in use for applications which seem far apart but are not. Who would imagine that the designer of glass for augmented reality has to cope with essentially the same issues as his predecessor working on glass for microscopy 100 years ago? However, there is a red thread connecting all this.

Both the red thread and different applications will be presented. First, the "red thread properties", the transmittancy, the refractive index, and the chromatic dispersion will be introduced. Remarkably, these properties are interrelated due to fundamental physics – not only for glass, but for any optical material (Kramers-Kronig relations [1]). Often, this makes it difficult to simultaneously adjust these properties to desired values.

Transmittancy. Preferably, optical glasses are made from oxides with high bandgaps so that only photons energetically corresponding to a frequency in the ultraviolet (UV) will be absorbed. These are, *e.g.*, SiO_2, B_2O_3, CaO etc. [1]. Low band gap, colouring impurities such as Fe_2O_3 are carefully avoided. With respect to Kramers-Kronig, however, a desired dispersion may require oxides with medium-size band gaps that will move the UV absorption edge close to the lower end of the visible spectrum (400nm) (see Fig. 1).

Chromatic Dispersion. Commonly, optical glasses are categorized in the Abbe diagram [2] according to n_d, the index at the Fraunhofer line d (587.6nm, yellow), and a characteristic figure for the chromatic dispersion, the Abbe number, which is defined by:

$$\boldsymbol{\nu}_d = \frac{n_d - 1}{n_F - n_C} \qquad (1)$$

The Abbe number increases with decreasing difference of the indices at the Fraunhofer lines F (486.1nm, blue) and C (656.3nm, red), *i.e.* with decreasing main dispersion ($n_F - n_C$). It is named after Ernst Abbe who in 1889 founded the Carl Zeiss foundation, the sole shareholder of the two companies Carl Zeiss AG and Schott AG.

Relative Partial Dispersion. As the relation between the refractive index and the wavelength is nonlinear, dispersion characterization requires a quantity which describes the degree of nonlinearity. A suited one is the relative partial dispersion $P_{d,C}$. It is the ratio between the yellow-to-red dispersion $n_d - n_C$ (partial dispersion) and the blue-to-red-dispersion $n_F - n_C$ (main dispersion):

$$\boldsymbol{P}_{d,C} = \frac{n_d - n_C}{n_F - n_C} \qquad (2)$$

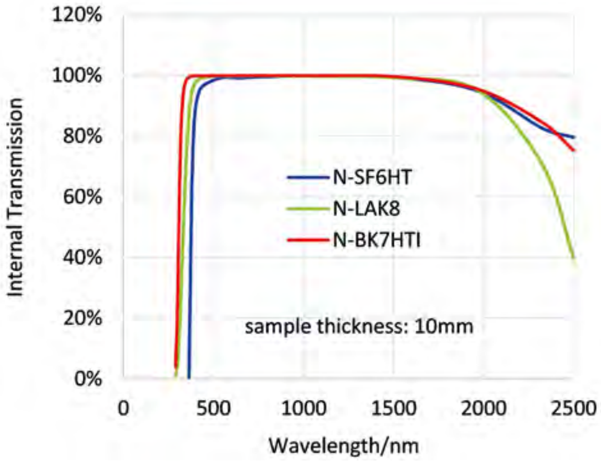

Figure 1: Internal transmission in UV, VIS, NIR for three glasses from SCHOTT AG.

For a linear wavelength dependence of the refractive index, $P_{d,C} = 0.4$ would hold. For real glasses, it is lower. Note that beside $P_{d,C}$, the analogously defined, but differently behaving $P_{g,F}$ is in use. g is the 435.8nm Fraunhofer line.

Refractive Index. Typical refractive index curves of optical glasses are given in Fig. 2. They are as expected from Kramers-Kronig [1]; one observes the following correlations (Figs. 1, 2):

#1. between the refractive index and the UV absorption edge: the higher the average index in the visible spectrum, the closer the UV absorption edge to the visible spectrum;

#2. between the UV absorption edge and main dispersion: the closer the UV absorption edge to the visible spectrum, the bigger the main dispersion;

#3. between the main dispersion and relative partial dispersion $P_{d,C}$: the bigger the main dispersion, the smaller the relative partial dispersion $P_{d,C}$.

The correlations #1-3 are what do make optical materials in the upper left of the Abbe diagram unfeasible! With the above background on optical glass, the challenges from optical design will now be discussed.

Challenges from Conventional Optics and Corresponding Glasses

Clear glass: enabler of optical imaging. Ca. 150 years before the first microscopes and telescopes were assembled in the early 17th century, the first clear glass had been made by Angelo Barovier. However, not knowing how to remove colouring impurities, he titrated the melt with MnO_2 until decolouration was reached [3]. As the absorption spectrum of MnO_2 is complementary to that of, *e.g.*, Fe_2O_3, a light grey absorption and thus an almost clear appearance may be obtained – a tricky, but smart approach. (The first application, however, was tableware.)

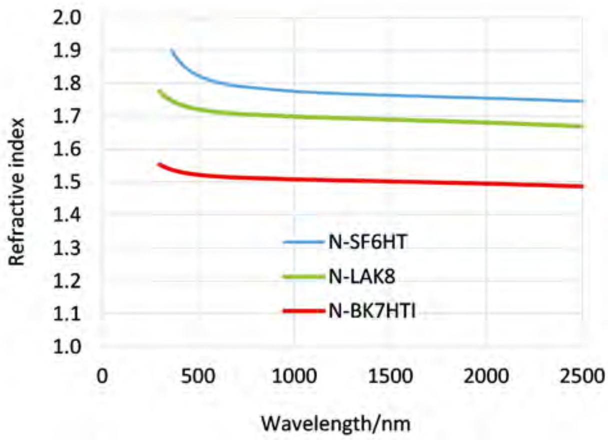

Figure 2: Refractive Index in UV, VIS, NIR for three glasses from SCHOTT AG.

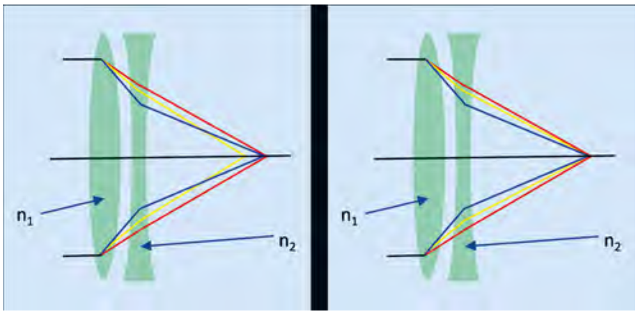

Figure 3: (left) Achromate with residual secondary colour. (Right) Apochromate.

These glasses were soda/potash-lime-silicates, called "crown glasses" after the manufacturing method [3]. The optical position in the Abbe diagram is denoted by "K".

Despite clear glass, the image quality of the early optical instruments was poor. Due to dispersion, "blue" rays are refracted stronger than "red" rays and have another focal length (primary colour). Different colours are imaged to different positions, with different magnifications, which gives rise to undesired colour fringes.

Achromates: solution to primary colour. In the middle of the 17th century, two element lenses were introduced, with the first element being a converging one with strong refractive power (short focal length), but small main dispersion, and the second element being a diverging one with small refractive power, but strong main dispersion.

By means of glass selection and lens element geometry, they are constructed such that (1) the resulting doublet is converging, but that (2) the strong main dispersion of the second element compensates the small main dispersion of the first element. (The dispersion by a converging element spreads colours, the dispersion by a diverging element recombines colours.) So coincidence of the "blue focus" and the "red focus" was reached (achromate, Fig. 3).

Expressed as a formula, the condition for achromatism is [3]:

$$0 = \frac{1}{f_{1,d} \cdot \nu_{1,d}} + \frac{1}{f_{2,d} \cdot \nu_{2,d}} \qquad (3)$$

The total focal length f_d (referring to $n = n_d$) for the doublet follows from the additivity rule for thin lens elements:

$$\frac{1}{f_d} = \frac{1}{f_{1,d}} + \frac{1}{f_{2,d}}. \qquad (4)$$

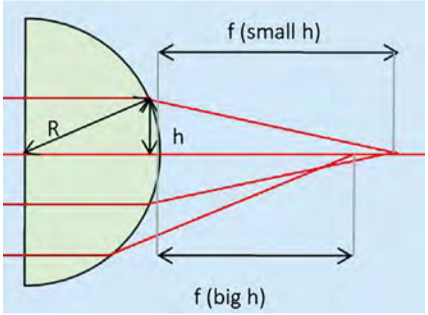

Figure 4: Spherical Aberration

By "$_{1,2}$" reference to the first or second lens element is indicated.

Fortunately, the high dispersion glass required had been invented some time before [3] by George Ravenscroft, who had introduced lead silicate for tableware, with its sparkling due to high chromatic dispersion being a very much desired feature. Consider, for instance, $PbO{\cdot}2SiO_2$. Its bandgap is 3.1 eV which corresponds to 400nm [3]. With correlation #2 (the closer the UV absorption edge to the visible, the bigger the main dispersion), a high dispersion glass can be expected. Such low Abbe number glasses are called "flints". Two names are attached to the first achromates: Chester Moore Hall (made the invention), and John Dolland (got the patent and made the money) [3].

Today, lead-free alternatives are often preferred. So beside the lead silicates with the acronym "SF", the lead- and arsenic-free "N-SF"-glasses, situated at the same positions in the upper right of the Abbe diagram, are available.

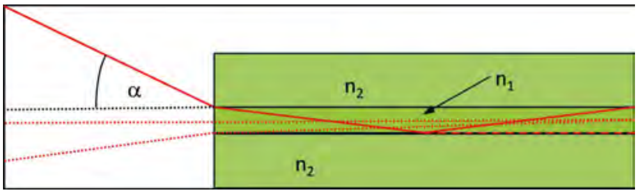

Figure 5: Lightguide

Apochromates: solution to residual secondary colour. In Fig. 3 (right), the yellow focal length is slightly smaller than that for blue and red. This is due to the nonlinear wavelength dependence of the refractive index, because of which the blue-to-yellow-dispersion is much bigger than the yellow-to-red-dispersion. If the spreading of wavelengths caused by the converging element is to be compensated by the diverging element, the ratio of the blue-to-yellow-dispersion to the yellow-to-red-dispersion must be the same for both elements. This is equivalent to equal relative partial dispersions.

However, correlation #3 says that the bigger the main dispersion, the smaller the relative partial dispersion $P_{d,C}$. is. So even if the main dispersion of the second element is strong enough to compensate the main dispersion of the first element, the partial dispersion will not be. This is why the yellow focal length is smaller than the one of red and blue. Therefore an apochromate with all colours in one focus did not yet exist when in the late 19th century, Otto Schott appeared on the scene.

Otto Schott could not override Kramers-Kronig. What he could do was to slightly scale up the index curve by increasing packing density. Thus, the average index and the main dispersion in the visible could be increased with neither moving the UV absorption edge nor affecting relative partial dispersion.

For this purpose, he switched from silicates to borates. $PbO{\cdot}2B_2O_3$, for instance, has a bigger band gap and a higher packing density than $PbO{\cdot}2SiO_2$ [3]. Starting with $PbO{\cdot}2B_2O_3$, he developed the borate flint S7 [3] ($n_D = 1.61$, $\nu_D = 44.3$) that, with

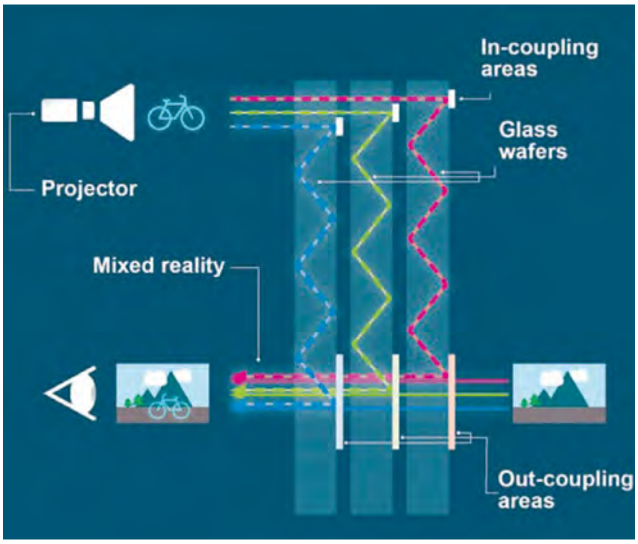

Figure 6: Three layers of glass in a waveguide for augmented reality (AR) glasses. Taken with permission from [6].

respect to relative partial dispersion, perfectly fitted to the high-potassium crown glass O13 [3] ($n_D = 1.52$, $\nu_D = 58$). This and other "special short flints" enabled the first apochromates, Fig. 3 (right). (In Otto Schott´s literature, the Fraunhofer line d is replaced with the nearby line D.)

First, chemical resistivity was an issue both for the borate flints and the high potassium crown glass. One approach by Otto Schott to settle this was to mix the two glass formers B_2O_3 and SiO_2, a pioneering step in glass development. Today, for example, the special short flint N-KZFS11 and the crown glass SCHOTT N-BK7® are borosilicates – such as numerous other optical and technical glasses.

Spherical Aberration: suppression requires high indices. Lens elements can easily be ground and polished by simple rotating devices [1], however, only spherical surfaces can thus be made. With them, the focus depends on the distance between rays and optical axis (longitudinal spherical aberration, Fig. 4). A second order calculation gives [1]:

$$f = \frac{R}{n-1} - \frac{h^2}{2R} \qquad (5)$$

So to suppress spherical aberration while maintaining f, a simultaneous increase of R and n is necessary. Due to Kramers-Kronig (correlation #1), this is especially challenging for low dispersion glasses.

Again Otto Schott was to find the solution, being the first to melt barium-containing glasses in an optical quality. With a band gap of 6eV, much higher than the one of PbO, BaO is well suited for low dispersion glasses. Although Kramers-Kronig prevents an ultra-high index, a moderately high index is achieved by the high packing density of, *e.g.*, glassy sanbornite $BaO{\cdot}2SiO_2$. Thus the barium crowns "BAK" as well as the (very) dense crowns "(S)SK" were launched. A later milestone

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Figure 7: FOV in AR glasses with different indices. Left: FOV with binocular vision. Centre: FOV with display glass, n = 1.5. Right: FOV for AR glass with n = 1.6 (smallest FOV) up to n = 2 (largest FOV). Taken with permission from [6].

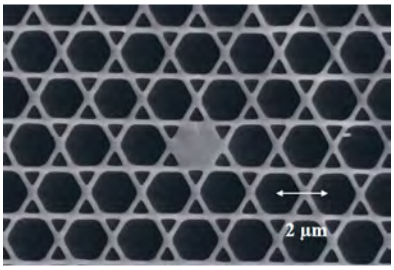

Figure 8: Cross section of a photonic crystal fibre manufactured by Schott AG.

concerning high index and low dispersion was lanthanum glass (George W. Morey, [1]).

Today´s high-end microscopes such as the ZEISS Axio Observer® offer sophisticated features like artificial-intelligence-based sample finders for biological samples to prevent them from the lasting illumination during a lengthy sample inspection by eye. The optical core is a high-end apochromate – with its roots going back to the extremely fruitful cooperation of Ernst Abbe, Carl Zeiss, and Otto Schott.

Novel Optics

"Lightguiding": key to the photonic revolution. Out of the numerous recent optical inventions, the most striking glass-related ones exploit the phenomenon of lightguiding. Already discovered in the 17th century by Johannes Kepler [4], total internal reflection had to wait until the 20th century with its first commercial use for illumination, imaging and communication.

Transmission is crucial. In conventional optics, light has to pass through centimeters of material only. Glass fibres for telecommunication, on the contrary, have to be so free of impurities that one could look through a several kilometer thick plate made of that glass. Manufacturing is by chemical vapour deposition [5]. Index and dispersion also play an important role. The acceptance angle of a lightguide, *i.e.* the maximum angle that is compatible with total reflection, is given by

$$\sin(\alpha) = \sqrt{n_1^2 - n_2^2} \qquad (5)$$

where n_1 is the core index and n_2 is the cladding index (see Fig. 5).

The desired indices depend on the application. For telecommunication, a low acceptance angle is preferred. Light entering at different angles would take different paths and thus cause an unwanted broadening of optical pulses. So no high indices are needed. Core and cladding are usually made from vitreous silica with certain dopants [5].

It is different for lightguiding in augmented reality (AR, [6]), Fig. 6. Here, the acceptance angle determines the field of view (FOV, [6]). The higher the index, the broader the field of view is. So high index glasses are required. Dispersion management is by different layers for different colours.

Photonic Crystals and Meta-Materials: exploiting the wave nature of light. Although the principles of lightguiding can be explained with ray optics, the complex behaviour of, *e.g.*, telecommunication fibres can only be understood considering the guided light as propagating modes, *i.e.* hybrid electromagnetic waves which are propagating along the fibre axis and standing waves in the perpendicular plane.

The wave character becomes particularly important if the confinement of light to the core is caused by interference in the cladding. That may occur at structures with a crystal-like order, so-called photonic crystals (Fig. 8) or at disordered structures, as it is the case for lightguiding with Anderson-localization where lightguiding is due to the interference of scattered light with the scatter centres lying closely together [7].

Photonic crystal fibres offer many different features, among them being special dispersion management for telecommunication, low-loss transport of laser power, and others [7].

Nevertheless, photonic crystal fibres are only a small part of what is generally possible with photonic crystals, *i.e.* ordered structures where periodicities with the magnitude of the wavelength cause special effects. Even more striking effects are possible with sub-wavelength structures with which very peculiar phenomena may be generated, *e.g.*, wave propagation and energy transport in opposite directions which is equivalent to a negative refractive index [7]. With respect to the highly sophisticated nanostructures involved, such materials will certainly not replace classical optical materials, but will offer highly welcome add-ons of the toolbox.

Conclusion

It is a long way from classical optical imaging to today´s optical applications like augmented reality. Nevertheless, glassmakers are all times confronted with similar issues concerning transmission, refractive index, and dispersion. This is due to the fact that said properties are inter-related by fundamental physical laws which prevent "once and for all times" solutions. On the other hand, these constraints are providing an ever-lasting challenge to find the limits of feasibility, employing all modern technologies like, *e.g.*, nanostructuring. ●

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- Wet paint thickness measurements, Pyrometry
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Rare earth doped fiber modules
3.9 µm pulsed laser
R G B pulsed fiber lasers

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