Chemical properties of optical glass: Test procedures, and considerations for design and assembly

Abstract

This paper will summarize the considerations of chemical stability of optical glasses, with an emphasis on design considerations relevant to common optomechanical systems.

It will consider the categorization of chemical stability into climatic (water) resistance, stain resistance, acid resistance, alkali resistance, and phosphate resistance, with descriptions of relevant test procedures. Then, a brief overview of the considerations with respect to fabrication and handling of lens systems will also be given.

Background: Review of Schott Technical Information [5]

The Schott technical paper "TIE-30: Chemical properties of optical glass" gives an overview of the methods used by Schott to characterize its optical-glass products for the purpose of writing specifications. First of all, the paper briefly describes the chemical principles behind corrosion of optical glasses. SiO_2, Al_2O_3, TiO_2, and rare-earth oxides are poorly soluble in aqueous and acidic solutions, so they are not highly susceptible to leaching and local corrosion. On the other hand, alkali and alkali earth oxides are more soluble and typically lead to formation of corroded layers. A thickness of 0.1 µm is used as the threshold for a significant chemical change resuilting from acid, alkali, or phosphate exposure. Next, the report gives descriptions of each test procedure and the corresponding inspection of the tested element. For climatic resistance, the test elements are placed in an atmosphere saturated with water vapor. The temperature is cycled between 40°C and 50°C with a period of one hour. The elevated temperature accelerates the aging process, while the temperature cycling is needed to produce condensation. The test elements are left in the climatic chamber for a total of 30 hours. The surface of the element is then observed using a spherical hazemeter to determine the level of transmission haze and the increase in haze resulting from the aging process, as given in Table 1.

CR class	1	2	3	4
Change in transmission	<0.3%	≥0.3%	≥1.0%	≥2.0%
Haze (ΔH)	N/A	<1.0%	<2.0%	N/A

Table 1. Criteria for climatic resistance (CR) classification. Adapted from Table 2.1 in ref [5]

As examples of glasses in the worst CR class (class 4), the report gives KZFS12, N-LAK21, N-SK14, and N-SK16. This is an important concern in the design of achromatic lenses and other multi-element lenses, where such glasses are common; an example will be discussed later.

Next, the report discusses stain resistance, defining it to describe the effect that results when weakly acidic aqueous solutions come in direct contact with the glass surface. Stain resistance is not necessarily coupled to climatic or acid resistance; some PSK and LaK glasses appear to form no stains in the stain-resistance test because a layer of glass is completely etched away without stain formation. The test procedure involves the pressing of the test sample into a cuvette in which a spherical depression of up to 0.25 mm depth is loaded with a few drops of the test solution so that the solution forms a film over the surface of the glass). Test solution I consists of a standard (unbuffered) acetate with pH = 4.6, while test solution II is a sodium acetate buffer with pH = 5.6.

The test element is left in contact with the solution at 25°C temperature until the first brown-blue interference stain occurs; the time is used to determine the stain resistance class as given in Table 2, below. If no interference stain is observed after 100 hours of exposure, the glass is classified as FR 0.

FR class	0	1	2	3	4	5
Test solution	I	I	I	I	II	II
Time (h)	100	100	6	1	1	0.2
Color change	no	yes	yes	yes	yes	yes

Table 2. Criteria for stain resistance (FR) classification. Adapted from Table 3-1 in ref [5]

Examples of glasses with poor stain resistance include SF57, SF66 (FR 5), N-KZFS2, and N-SK16 (FR 4).

The tests for acid resistance involve a larger volume of solution with an optionally lower (more acidic) pH than that of the stain resistance test, to allow for gross decomposition of the glass to be observable. The first test solution is a 0.5 mol/L nitric acid solution with pH = 0.3, and the second is a standard acetate solution with pH = 4.6 (the same as test solution I for stain resistance) The former is most commonly used, in order to achieve a sufficiently aggressive reaction with common glasses; the latter is used for less acid-resistant glasses so as to allow a reasonably long duration of testing. Physically, acid resistance is limited by the concentration and distribution of the sparingly soluble substances within the glass. In some cases, it is impossible to include a sufficient quantity of such solutes while still maintaining the desired optical properties. This makes the glass poorly acid-resistant. The test proceeds until a layer thickness of 0.1 µm is removed. (Since this does not necessarily involve the formation of an interference layer, direct dimensional measurements before and after the acid treatment are needed. The Schott report does not recommend a specific method for such measurements.) The acid resistance class (SR) is given as in Table 3.

SR	1	2	3	4	5		51	52	53
pH	0.3					4.6			
Time (h)	>100	10-100	1-10	0.1-1	<0.1	>10	1-10	0.1-1	<0.1

Table 3. Criteria for acid resistance class (SR). Adapted from Table 4-1 in ref [5]

The acid resistance is fully specified as the the SR number followed by an additional digit, separated by a period, that indicates the surface change visible to the unaided eye. Visible surface changes resulting from acid exposure are classified as follows:

- 0 = no visible changes
- 1 = clear but uneven surface
- 2 = interference color(s) visible
- 3 = firmly adhered layer of cloudy leaching material
- 4 = thick, loosely adhering layer of material

As an example of a glass in the worst possible acid resistance rating (53.4), the report gives SF66. The report mentions 6 examples of glasses rated 53.3, and as an example of rating 53.2 it gives N-LAK21.

Finally, the report discusses alkali and phosphate resistance. These chemical classes are especially relevant to the assembly and maintenance of practical systems due to their presence in grinding and polishing compounds as well as soaps. Similarly to acid resistance, the alkali and phosphate resistance ratings are constructed in two parts, from an alkali or phosphate resistance class number, and a number describing surface change on the same scale previously mentioned. The alkali resistance class (AR) is obtained by application of a sodium hydroxide (NaOH) solution with concentration 0.01 mol/L and pH 12 at a temperature of 50°C; the phosphate resistance class (PR) is obtained by application of an alkaline solution of pentasodium triphosphate ($Na_5P_3O_{10}$) at 50°C. The class number for either alkali or phosphate resistance is given by the exposure time needed to remove a thickness of 0.1 µm, as in Table

4.

AR or PR	1	2	3	4
Time (h)	>4	1-4	0.25-1	<0.25

Table 4. Criteria for alkali resistance class (AR) and phosphate resistance class (PR). Adapted from Table 5-1 in ref [5]

Examples given of glasses with alkali rating 4.3 are KZFS12, KZFSN4, KZFSN5, N-KZFS2, and N-LAK21. N-KZFS2 and SF66 have phosphate resistance rating 4.2; 13 glasses have phosphate resistance rating 4.3.

Sidebar: List of relevant ISO standards

- Climatic resistance: ISO/CD 13384 (proposal), "Raw optical glass – Testing of the climate resistance CR (resistance to humidity) at temperatures changing between 40°C and 50°C and classification"
- Stain resistance: No applicable standard
- Acid resistance: ISO 8424, "Raw optical glass – Resistance to attack by aqueous acidic solutions at 25°C – Test method and classification"
- Alkali resistance: ISO 10629, "Raw optical glass – Resistance to attack by aqueous alkaline solution at 50°C – Test method and classification"
- Phosphate resistance: ISO 9689, "Raw optical glass – Resitance to attack by aqueous alkaline phosphate-containing detergent solutions at 50°C – Testing and classification"

Discussion: Design and fabrication considerations of glass choice in a multi-lens system

For actual testing in a laboratory or fabrication line, one could replicate the testing procedures as given by Schott and the original ISO specifications they cite (see Sidebar, above). One would in practice test a random sampling of glass blanks to ensure that they are statistically likely to meet the manufacturer's specifications, and perform similar statistical sampling at later stages of the assembly, including the finished product.

When fabricating an existing design that contains glasses of poor chemical resistance, appropriate precautions include the aforementioned testing as well as caution taken in assembly to ensure that the worker's perspiration as well as aqueous solutions of laboratory chemicals do not come in contact with the sensitive element. This may include the use of gloves when manual handling is necessary; automated assembly machines should resolve such issues for highly critical systems where the cost and accuracy requirements justify it.

For comparison, examples of glasses with good chemical resistance include BK7, a borosilicate crown glass with CR 2, SR 1, and AR 1.[1] (The revised N-BK7 composition instead has AR 2, and is additionally specified as FR 0 and PR 2.3.[3]) The well-rounded chemical stability of BK7 and its cost-performance ratio explain its popularity as a material for visible-light lens elements. Another glass with comparable chemical stability is Borofloat, with class 1 climatic and acid resistance and class 2 alkali resistance.[2] However, its official description from Schott implies that it is optimized primarily for mechanical/thermal stability, and in its current form it is not intended for use as a lens material. Its primary optical application is in the flat-plate covers of photovoltaic cells.[4]

Let us consider a typical achromatic doublet lens, used perhaps as the first converging lens in a monocular magnifier. The front, convex element is typically made of a crown glass such as BK7 or N-BK7. The rear, concave element is of a flint glass, which has higher dispersion. The only design feature relevant to this discussion is that these two elements are cemented together with the positive element exposed to the exterior (Fig. 1). It is expected that the interface between the elements, as well as that between the doublet and the barrel, have adhesive applied uniformly enough that no irregularities or holes exist to serve as starting points for chemical attack. We assume the chemical strength of the adhesive is no worse than that of either glass.

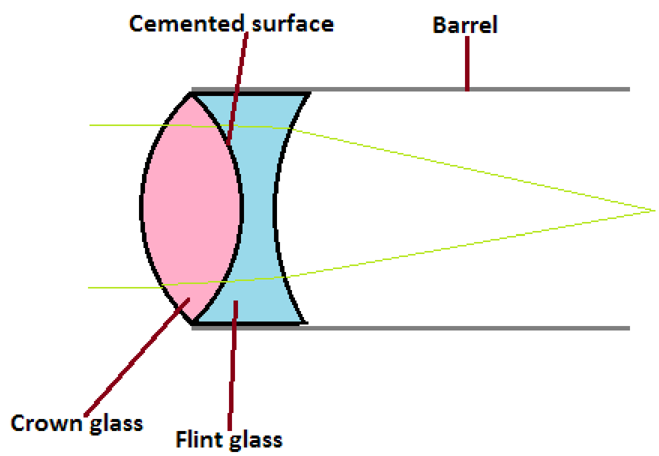

Fig. 1. Schematic of achromatic doublet lens with mount. The right end of the barrel is intended to be sealed by the presence of additional (chemically insensitive) lenses, a diaphragm, and/or connection to a larger optical system. (Illustration: Own work)

One flint glass with relatively high dispersion is KZFS12, with ν_d = 36.29; compare the lower dispersion ν_d= 64.17 for N-BK7.[3] The borate flint (KZFS) class has generally poor chemical strength in all categories. Glasses containing both borates and at least 20 molar percent lanthanum perform better, but such glass compositions are not routinely manufactured by Schott. In the final assembled system, only the convex BK7 element comes directly in contact with environmental influences such as atmospheric moisture. However, during assembly, great care must be taken to avoid exposing the KZFS12 element to high levels of moisture (CR 4), strong acids (SR 53.3), or any alkalis or phosphates (AR 4.3, PR 4.3), especially at elevated temperatures. As KZFS12 is rated at FR 1, weaker acids are not of significant concern. Of course, skin contact must still be avoided in order to prevent fingerprints and other organic contamination.

The required assembly conditions can be achieved by using gloves for all human handling of the negative element. The requirements on these gloves are not particularly demanding, due to the glass's good stain resistance; ordinary latex gloves are sufficient provided that the environment is suitably controlled to eliminate sources of steam and strong acids/alkalis. Additionally, automated assembly machinery may be needed for the cementing of the elements and subsequent installation into the barrel. The handling requirements become less stringent once the system is fully assembled. At that point, the priority is to prevent leaks of steam or aqueous chemical solutions from entering the space of the barrel, where they would contaminate the back surface of the negative lens. This requirement is easy to achieve for common visual optics, provided that the barrel is a single solid piece or that the system is operated in a suitably controlled environment.

Finally, computer simulations and accelerated-aging experiments on prototypes may be vital tools to evaluate the reliability of the system. If screw threads are present in the system, either as lens mounts or to join barrel segments, such tests may be valuable to determine the thread dimensions and machining grade necessary to control gas leakage. Other special situations that warrant attention may include:

- Demanding operating environments, such as high temperatures in combination with chemical fumes
- Barrel designed to be disassembled and reassembled while the system is in use
- Redesign of the lens as a dialyte lens, in which the separation between the lens elements exposes both sides of each to environmental attack
- Constraints in the material choice; for example, operation at UV wavelengths where BK7 is

unsuitable due to poor transmission (< 300 nm), or when new innovations make some other glass or polymer composition more economical

On the other hand, if the lens were redesigned as a cemented triplet, the central element would not be directly exposed to environmental stresses under proper mounting, so the chemical requirements on that element would be relatively lax, and the burden would shift to the cementing process.

Conclusions

An overview of the Schott technical report "TIE-30: Chemical properties of optical glass" is given. The test procedures described in the report are summarized, and the chemical parameters of representative glasses are evaluated with regard to said procedures. Also, the considerations of chemical stability for the design and assembly of a lens system are discussed.

References

[1] "Bk7 Optical Glass Flats from VPG." http://www.vpglass.com/optical_glass/bk7_glass.html. Volume Precision Glass, Inc. Accessed 1 Dec 2013.

[2] "Borofloat Optical Glassfrom *[sic]* VPG." http://www.vpglass.com/optical_glass/borofloat_glass.html. Volume Precision Glass, Inc. Accessed 1 Dec 2013.

[3] "Optical Glass – Description of Properties." Schott, June 2003. Supplied by University of Arizona, OPTI 521 class notes, 2013. pp. 6-33.

[4] "SCHOTT BOROFLOAT® 33 Borosilicate Glass." http://www.us.schott.com/borofloat/english/index.html. Schott North America, Inc., 2013. Accessed 1 Dec 2013.

[5] "TIE-30: Chemical properties of optical glass." Technical Information – Optics for Devices. Schott, July 2004. Supplied by University of Arizona, OPTI 521 class notes, 2013. pp. 1-9.