

SCHOTT Technical Glasses

Physical and technical properties



SCHOTT
glass made of ideas

Foreword

A part from its application in optics, glass as a technical material exerted a formative influence on the development of important technological fields such as chemistry, pharmaceuticals, automotive, optoelectronics and renewable energy such as solar thermal or photovoltaics. Traditional areas of technical application for glass, such as laboratory apparatus, flat panel displays and light sources with their various requirements on chemicophysical properties, led to the development of a great variety of special glass types. By new fields of application, particularly in optoelectronics, this variety of glass types and their modes of application have been continually enhanced, and new forming processes have been developed. The hermetic encapsulation of electronic components gave decisive impetus to development activities. Finally, the manufacture of high-quality glass ceramics from glass has opened entirely new dimensions, setting new standards for various technical applications.

To continuously optimize all commercial glasses and glass articles for existing applications and to develop glasses and processes for new applications is the constant endeavor of SCHOTT research. For such dynamic development it is mandatory to be in close contact with the customers and to keep them as well informed as possible about glass.

SCHOTT Technical Glasses offers pertinent information in concise form. It contains general information for the determination and evaluation of important glass properties and also informs about specific chemical and physical characteristics and possible applications of the commercial technical glasses produced by SCHOTT. With this brochure we intend to assist scientists, engineers, and designers in making the appropriate choice and optimum use of SCHOTT products.

Users should keep in mind that the curves or sets of curves shown in the diagrams are not based on precision measurements but rather characterize and illustrate the typical property profiles of the respective glasses or glass types. Up-to-date characteristic values of particular glasses are to be found in the tables of this brochure or in separate data sheets.

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1	Types of Technical Glasses	5
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Evaluation and Significance of Important Glass Properties

2	Chemical Resistance of Glasses	6
	2.1 Chemical reaction mechanisms with water, acids, and alkaline solutions	6
	2.2 Determination of the chemical stability	7
	2.3 Significance of the chemical stability	9
3	Mechanical and Thermal Properties	11
	3.1 Viscosity	11
	3.2 Strength	12
	3.3 Elasticity	14
	3.4 Coefficient of linear thermal expansion	14
4	Electrical Properties	16
	4.1 Volume resistivity	16
	4.2 Surface resistivity	16
	4.3 Dielectric properties	17
	4.4 Dielectric strength	18
5	Optical Properties	19
	5.1 Refraction of light	19
	5.2 Stress birefringence	20
	5.3 Light transmittance	20

Special Properties and Applications of Technical Glasses

6	Chemically Highly Resistant Glasses	21
	6.1 DURAN®	21
	6.2 SCHOTT SUPRAX®	22
	6.3 SCHOTT FIOLAX®	22
	6.4 SCHOTT BOROFLOAT® 33 & SUPREMAX® 33	23
7	Sealing Glasses	24
	7.1 General information	24
	7.2 Types of sealing glasses	24
	7.3 Compression seals	26
	7.4 Ceramic glass seals	27
	7.5 Intermediate sealing glasses	28
	7.6 Glass and Glass Ceramic Sealants for Solid Oxide Fuel Cells (SOFC)	30
8	Solder Glasses	31
9	Passivation Glasses	35
10	Glass Ceramics	37
	Glass Types	39
	Literature	42



Fig. 1. *Ingredients for the production of special glasses*

1. Types of Technical Glasses

In the following, technical glasses are understood to be special glasses manufactured in the form of tubes, rods, hollow vessels and a variety of special shapes, as well as flat glass and granulate for use mainly in chemistry, laboratory technology, pharmaceuticals, optoelectronics, and household appliance technology.

Glasses for purely optical applications are usually distinguished from these technical glasses by their special manufacturing processes and by their special compositional ranges.

For the purposes of classification, the multitude of technical glasses can be roughly arranged in the following four groups, according to their oxide composition (in weight percent). It should be noted, however, that certain glasses fall between these groups, and others completely outside of the groups, and therefore cannot be classified as belonging to these types.

Borosilicate glasses

Characteristic of this type is the presence of substantial amounts of silica (SiO_2) and boric oxide ($\text{B}_2\text{O}_3 > 8\%$) as glass network formers.

The amount of boric oxide affects the glass properties in a particular way. Apart from the highly resistant varieties (B_2O_3 up to a maximum of 13%) there are others that – due to the different way in which the boric oxide is incorporated into the structural network – have only low chemical resistance (B_2O_3 content over 15%). Hence we differentiate between the following subtypes.

Non-alkaline-earth borosilicate glass (borosilicate glass 3.3)

The B_2O_3 content for borosilicate glass is typically 12–13% and the SiO_2 content over 80%. High chemical durability and low thermal expansion ($3.3 \times 10^{-6}/\text{K}$) – the lowest of all commercial glasses for large-scale technical applications – make this a multitasking glass material.

High-grade SCHOTT borosilicate flat glasses are used in a wide variety of industries, mainly for technical applications that need either good thermal resistance, excellent chemical durability, or high light transmission in combination with a pristine surface quality.

Other typical applications for different forms of borosilicate glass include glass tubing, glass piping, glass containers, etc. especially for the chemical industry.

BOROFLOAT® 33, SUPREMAX® 33 and DURAN®, belong to this glass family.

Alkaline-earth containing borosilicate glasses

In addition to about 75% SiO_2 and 8–12% B_2O_3 , these glasses contain up to 5% alkaline earths and alumina (Al_2O_3). To this subtype of slightly softer glasses (as compared with non-alkaline-earth borosilicate glass),

which have thermal expansions between $4.0\text{--}5.0 \times 10^{-6}/\text{K}$, belong the chemically highly resistant varieties FIOLEX® 8412 and 8414 (“neutral glasses”), and SUPRAX® and 8488.

High-borate borosilicate glasses

Glasses containing 15–25% B_2O_3 , 65–70% SiO_2 , and smaller amounts of alkalis and Al_2O_3 as additional components, have low softening points and low thermal expansion. Sealability to metals in the expansion range of tungsten-molybdenum and high electrical insulation are their most important features. The increased B_2O_3 content reduces the chemical resistance; in this respect, high-borate borosilicate glasses differ widely from non-alkaline-earth and alkaline-earth borosilicate glasses.

Examples: 8245, 8250, 8271, 8337B, 8487.

Alkaline-earth aluminosilicate glasses

Characteristically, these glasses are free of alkali oxides and contain 15–25% Al_2O_3 , 52–60% SiO_2 , and about 15% alkaline earths. Very high transformation temperatures and softening points are typical features. Main fields of application are glass bulbs for halogen lamps, display glasses, high-temperature thermometers, thermally and electrically highly loadable film resistors and combustion tubes. Examples: Halogen lamp glass types 8252 and 8253.

Alkali-lead silicate glasses

Such glasses typically contain over 10% lead oxide (PbO). Lead glasses containing 20–30% PbO , 54–58% SiO_2 and about 14% alkalis are highly insulating and therefore of great importance in electrical engineering. They are used in lamp stems.

Lead oxide is also of great importance as an X-ray protective component (radiation shielding glass and cathode ray tube components).

Alkali alkaline-earth silicate glasses (soda-lime glasses)

This is the oldest glass type. It comprises flat glasses (window glass) and container glasses, which are produced in large batches. Such glasses contain about 15% alkali (usually Na_2O), 13–16% alkaline earths ($\text{CaO} + \text{MgO}$), 0–2% Al_2O_3 and about 71% SiO_2 .

Variants of the basic composition can also contain significant amounts of BaO with reduced alkali and alkaline-earth content. Example: 8350.

Also belonging to this group are glasses with higher BaO content for X-ray protection such as used in cathode ray tube components. Example: TV-panel glass 8056. On a broader plane, certain crystal glasses (drinking glasses) can also be included.

2. Chemical Stability of Glasses

Characteristically, glass is highly resistant to water, salt solutions, acids, and organic substances. In this respect it is superior to most metals and plastics. Glass is attacked to a significant degree – particularly at higher temperatures – only by hydrofluoric acid, strong alkaline solutions, and concentrated phosphoric acid.

Chemical reactions with glass surfaces, induced by exchange, erosion or adsorption processes, can cause most diversified effects, ranging from virtually invisible surface modifications to opacity, staining, thin films with interference colors, crystallization, holes, rough or smooth ablation, to name but a few. These changes are often limited to the glass surface, but in extreme cases they can completely destroy or dissolve the glass. Glass composition, contact medium, and operating conditions will decide to what extent such chemical attacks are technically significant.

2.1 Chemical reaction mechanisms with water, acids, and alkaline solutions

Chemical stability is to be understood as the resistance of the glass surface to chemical attack by defined agents, whereby temperature, exposure time, and the condition of the glass surface play important roles.

Every chemical attack on glass involves water or its dissociation product, i.e., H^+ or OH^- ions. For this reason, we differentiate between hydrolytic (water), acid and alkali resistance. By water or acid attacks, small amounts of (mostly mono- or divalent) cations are leached out. In resistant glasses a very thin layer of silica gel then forms on the surface, which normally inhibits further attack (Figure 2a, b). Hydrofluoric acid, alkaline solutions and in some cases phosphoric acid, however, gradually destroy the silica framework and thus ablate the glass surface in total (see Figure 2c). In contrast, water-free (i.e., organic) solutions do not react with glass.

Chemical reactions are often increased or decreased by the presence of other components. Alkali attack on glass is thus hindered by certain ions, particularly those of aluminum. On the other hand, complex-forming compounds such as EDTA, tartaric acid, citric acid, and others, will increase the solubility. In general terms, the glass surface reacts with solutions which induce small-scale exchange reactions and/or adsorptions. Such phenomena are observed, for example, in high-vacuum technology when residual gases are removed, or in certain inorganic-chemical operations when small amounts of adsorbed chromium, resulting from treatment with chromic acid, are removed.

Because acid and alkali attacks on glass are fundamentally different, silica-gel layers produced by acid attack obviously are not necessarily effective against alkali solutions and may be destroyed. Conversely, the presence of ions that inhibit an alkali attack does not necessarily represent

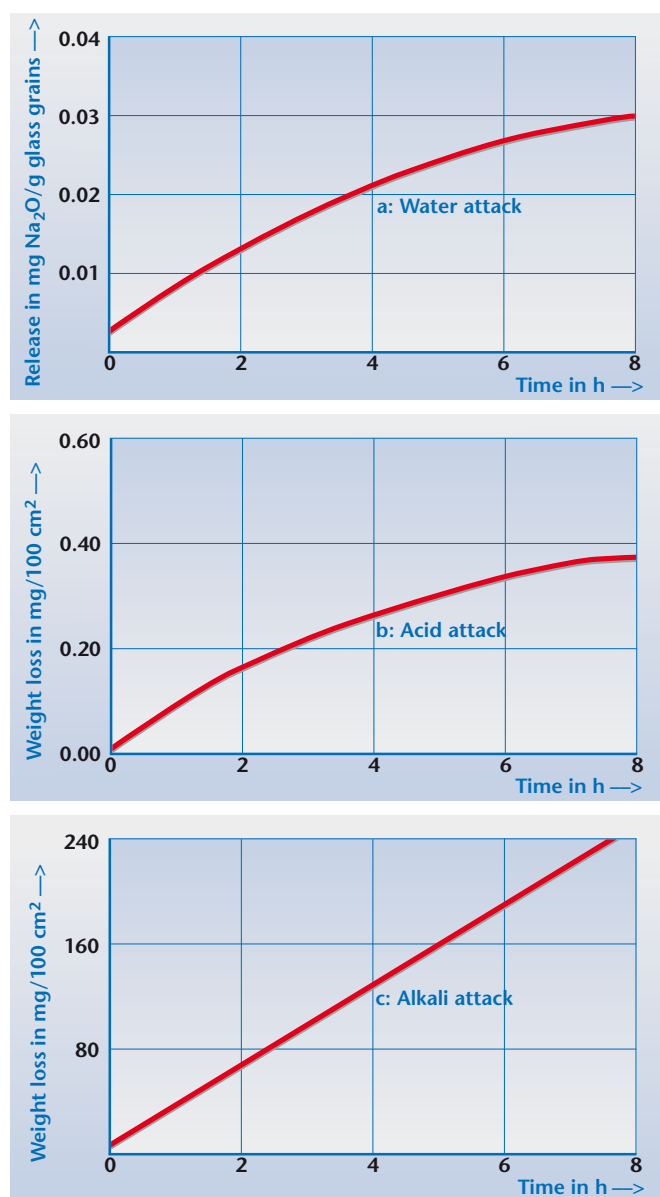


Fig. 2. Attack by water, acids and alkaline solutions on chemically resistant glass as a function of time

protection against acids and water. The most severe chemical exposure is therefore the alternating treatment with acids and alkaline solutions. As in all chemical reactions, the intensity of interaction increases rapidly with increasing temperature (Figures 31 and 33).

In the case of truly ablative solutions such as hydrofluoric acid, alkaline solutions, or hot concentrated phosphoric acid, the rate of attack increases rapidly with increasing concentration (Figure 3). As can be seen in Figure 4, this is not true for the other frequently applied acids.

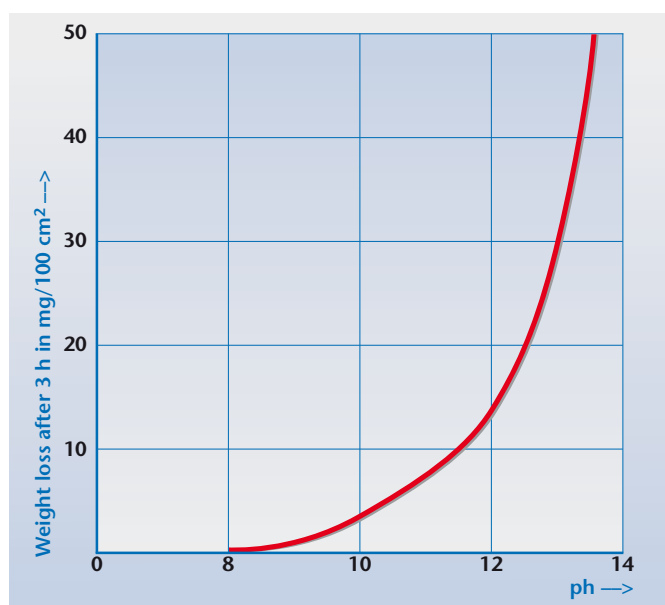


Fig. 3. Alkali attack on DURAN®/BOROFLOAT® 33/SUPREMAX® 33 related to pH value at 100 °C

2.2 Determination of the chemical stability

In the course of time, many analysis methods have been suggested for determining the chemical stability of glass. In most cases it is the glass surface that is analyzed either in its “as delivered” condition (with the original fire-polished surface) or as a basic material with its fire-polished surface removed by mechanical or chemical ablation, or after crushing.

The standardized DIN* test methods, which are universally and easily applicable, are the most reliable analysis methods. They include the determination of hydrolytic resistance (by two grain-titration methods and one surface method), of acid resistance to hydrochloric acid, and of alkali resistance to a mixture of alkaline solutions.

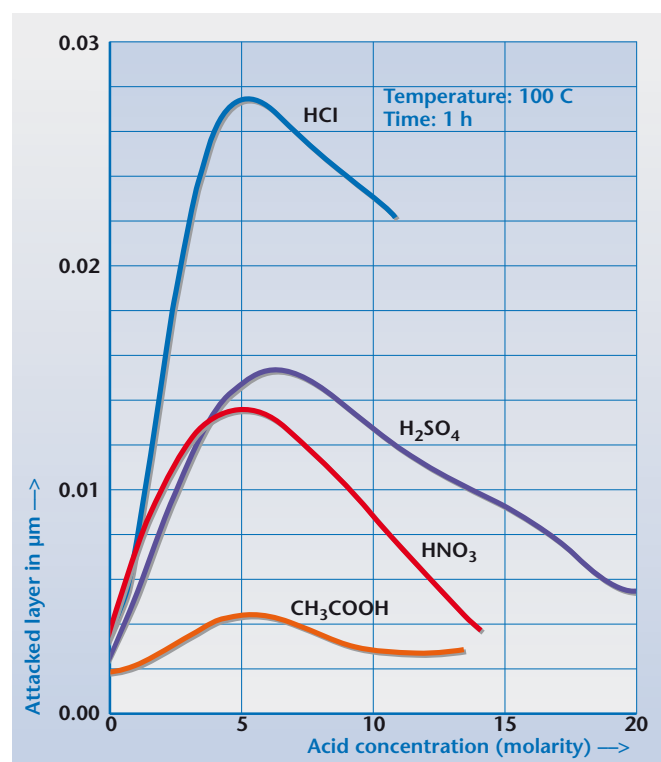


Fig. 4. Acid attack on DURAN®/BOROFLOAT® 33/SUPREMAX® 33 as a function of concentration

2.2.1 Hydrolytic resistance (water resistance)

Grain-titration method A

(after leaching at 98 °C, according to DIN ISO* 719; testing of glass as a material)

An amount of 2 g of powdered glass with 300–500 µm (ISO) grain size is heated with 50 ml water for one hour in a boiling water bath. The extracted alkali is then titrated with hydrochloric acid, $c(\text{HCl}) = 0.01 \text{ mol/l}^{**}$, using methyl red sodium as indicator. On the basis of the acid

Table 1. Hydrolytic classes of DIN ISO 719

Hydrolytic classes	Acid consumption of 0.01 mol/l hydrolytic acid per g glass grains ml/g	Base equivalent as Na ₂ O per g glass grains µg/g	Possible designation
1	up to 0.10	up to 31	very high resistant glass
2	above 0.10 up to 0.20	above 31 up to 62	high resistant glass
3	above 0.20 up to 0.85	above 62 up to 264	medium resistant glass
4	above 0.85 up to 2.0	above 264 up to 620	low resistant glass
5	above 2.0 up to 3.5	above 620 up to 1085	very low resistant glass

* = International Organization for Standardization

** = The old term for concentration in “normal solutions N” has been replaced by “mol/l” in the SI system.



Fig. 5. DURAN® borosilicate glass in the laboratory

consumption (or its alkali equivalent) the glass is allocated to one of the five hydrolytic classes given in Table 1. The hydrolytic classes shown in Table 12 (on page 36/37) were determined using the above method.

Grain-titration method B

(after leaching at 121 °C, according to DIN ISO 720; testing of glass as a material)

In this method, which originated in the USA and which is particularly suitable for highly resistant glasses, 10 g of powdered glass (grain size 300–425 µm) is leached with 50 ml of water in an autoclave for 30 min at 121 °C. The extracted alkali is then titrated with hydrochloric acid, $c(\text{HCl}) = 0.02 \text{ mol/l}$, using methyl red sodium as indicator. Here, too, the acid consumption is a measure of the hydrolytic resistance. Presently, no allocation into classes exists for DIN ISO 720.

Surface test method

(at 121 °C, according to DIN 52 339 (1980) (Part 1 = European Pharmacopeia)).

Grain-titration methods are always carried out on crushed-glass samples and the glass is tested as a material. With the surface test method, in contrast, the water resistance of the

surface can be determined in its “as delivered” state. In this method, new, undamaged vessels (e.g. flasks, test tubes, vials, ampoules) are filled with water and heated for 60 min at 121 °C in an autoclave. The leaching solution is then titrated with hydrochloric acid, $c(\text{HCl}) = 0.01 \text{ mol/l}$, using methyl red sodium as indicator. Distinguished according to volume, the containers are classified on the basis of the amount of acid required for neutralization.

The values gained by this method indicate not only the behavior of the glass material as such, but also reflect possible modifications induced in the glass surface during hot forming. Therefore, these values are not quoted in the tables included in this publication.

2.2.2 Acid resistance, according to DIN 12116

The glass surface to be tested is boiled for 6 h in 20% hydrochloric acid [$c(\text{HCl}) = 6 \text{ mol/l}$], and the loss in weight is determined in $\text{mg}/100 \text{ cm}^2$. Using the half loss in weight, the glasses are then classified as follows:

Table 2. Acid classes

Acid class	Designation	Half loss in weight after 6 h $\text{mg}/100 \text{ cm}^2$
1	highly acid resistant	up to 0.7
2	acid resistant	above 0.7 up to 1.5
3	slight acid attack	above 1.5 up to 15
4	high acid attack	above 15

Acid classes for glasses manufactured by SCHOTT are listed in Table 12.

2.2.3 Alkali resistance, according to DIN ISO 695

To determine the alkali resistance, glass surfaces are subjected to a 3 h treatment in boiling aqueous solution consisting of equal volumes of sodium hydroxide, $c(\text{NaOH}) = 1 \text{ mol/l}$ and sodium carbonate, $c(\text{Na}_2\text{CO}_3) = 0.5 \text{ mol/l}$. The loss in weight is then determined, and the glasses are classified as follows:

Table 3. Alkali classes

Alkali class	Designation	Loss in weight after 3h $\text{mg}/100 \text{ cm}^2$
1	low alkali attack	up to 75
2	slight alkali attack	above 75 up to 175
3	high alkali attack	above 175

Alkali classes for glasses manufactured by SCHOTT are listed in Table 12.

The following borosilicate glasses have particularly high chemical resistance: DURAN®/BOROFLOAT® 33/ SUPREMAX® 33 (8330), SUPRAX® (8488), FIOLAX® clear (8412), FIOLAX® amber (8414) and PYRAN® S (8341); see Table 4, p. 23.

2.3 Significance of the chemical stability

2.3.1 Corrosion resistance in chemical plant applications

For such applications, the glasses must be resistant to the various chemical solutions to such a degree that manifold reactions can take place without running the risk of damaging the laboratory glass or the equipment by strong ablation. Moreover, no interfering amounts of glass components must be released into the reaction mixture. Attack by acids is of particular importance, both in laboratories and in chemical technology. Here, borosilicate glasses with their high acid resistance are superior to other materials. Up to the boiling point, their reactivity is very low; it then increases with increasing acid concentration, but decreases again at higher concentrations (Figure 4). The alkali attack, in contrast, increases exponentially with increasing alkali concentration (Figure 3).

A comparison of the effect of the alkaline mixture (concentration of alkaline components about 1 mol/l) with the effect of 6 mol/l hydrochloric acid (the most aggressive acid used in acid resistance tests) under standard conditions shows that the alkali attack increases by a factor of 1000 after extended exposure.

2.3.2 Release of glass constituents

In various processes of chemical technology, pharmaceuticals, and laboratory work, the material glass is expected to release no constituents (or a very minimum) into the reacting solutions or stored specimens.

Because even highly resistant materials such as non-alkaline-earth and alkaline-earth borosilicate glasses do react to a very small degree with the surrounding media, the fulfilment of this requirement is a question of quantity and detection limits. Concentrations of 10^{-6} – 10^{-9} (i.e., trace amounts), which are measurable today with highly sophisticated analytical instruments, can be released even from borosilicate glasses in the form of SiO_2 , B_2O_3 , and Na_2O , depending on the conditions. However, solutions in contact with high-grade colorless DURAN® laboratory glass will not be contaminated by Fe, Cr, Mn, Zn, Pb, or other heavy-metal ions.

2.3.3 Undesirable glass surface changes

When an appreciable interaction between a glass surface and aqueous solutions occurs, there is an ion exchange in which the easily soluble glass components are replaced by H^+ or OH^- ions. This depletion of certain glass components in the surface leads to a corresponding enrichment in silica, which is poorly soluble, and thus to the formation of a so-called silica-gel layer. This layer proves, in most cases, to be more resistant than the base glass. When its thickness exceeds about 0.1–0.2 μm , interference colors caused by the different refractive indices of layer and base glass make this silica-gel layer visible to the unaided eye. With increasing layer thickness it becomes opaque and finally peels off, destroying the glass.

In the case of technical laboratory glass, the first stages are only a question of aesthetics. The functionality of the glass

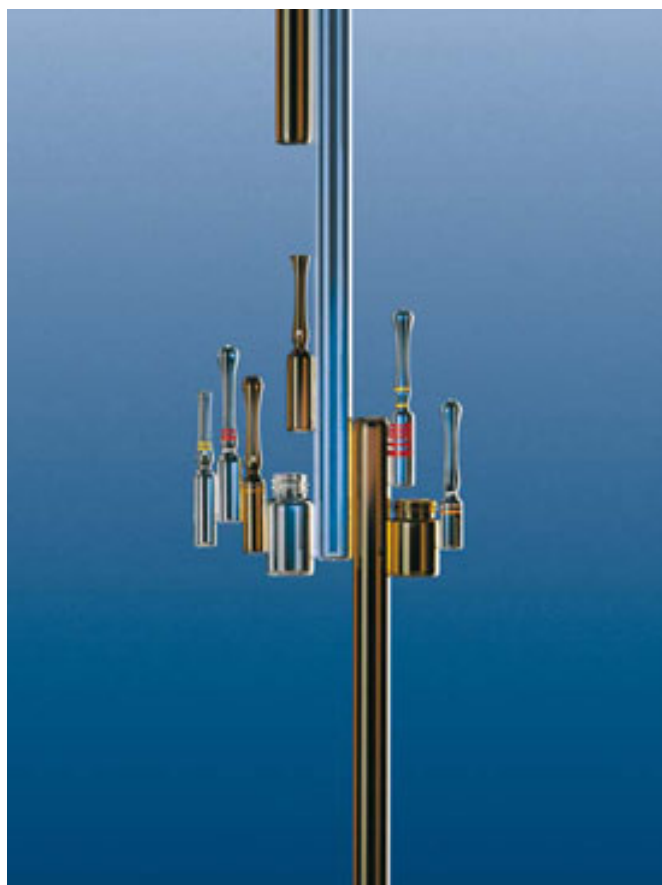


Fig. 6. Fiolax® vials and ampoules

is not influenced in any way. In optical glasses, however, interference colors and opacity are usually unacceptable, and in glasses for electrical engineering, applicability may be reduced. In the final stage of degradation, when the silica-gel layer peels off, the glass of course becomes useless for any application.

Between these stages there is a wide scope of possible surface modifications, some of which, although optically visible, are of no practical significance, whereas others must be considered.

In the case of less resistant glasses, small amounts of water (air moisture and condensation) in the presence of other agents such as carbon dioxide or sulfur oxides can lead to surface damage. In the case of sensitive glasses, hand perspiration or impurities left by detergents can sometimes induce strongly adhering surface defects, mostly recognizable as stains. If the contaminated glass surfaces are reheated (> 350 – 400°C), the contaminants or some of their components may burn in. Normal cleaning processes will then be ineffective and the whole surface layer has to be removed (e.g. by etching).



Fig. 7. Floating of borosilicate glass

2.3.4 Desirable chemical reactions with the glass surface (etching)

Very strong reactions between aqueous agents and glass can be used for fundamental cleaning of glass. The complete ablation of glass layers leads to the formation of a new surface.

Hydrofluoric acid reacts most strongly with glass. Because it forms poorly soluble fluorides with a great number of glass constituents, it is mostly only used in diluted form. The best etching effect is usually achieved when another acid (e.g., hydrochloric or nitric acid) is added. A mixture of seven parts by volume of water, two parts of concentrated hydrochloric acid ($c = 38\%$) and one part of hydrofluoric acid ($c = 40\%$) is recommended

for a moderate surface ablation of highly resistant borosilicate glasses. When chemically less resistant glasses (e.g. 8245, 8250) are exposed for five minutes to a stirred solution at room temperature, surface layers with thicknesses of $1 - 10 \mu\text{m}$ are ablated, and a transparent, smooth, completely new surface is produced.

Glasses can also be ablated with alkaline solutions, but the alkaline etching process is much less effective.

3. Mechanical and Thermal Properties

3.1 Viscosity

Between melting temperature and room temperature, the viscosity of glasses increases by 15–20 orders of magnitude. Within this viscosity range, glasses are subject to three different thermodynamic states:

1. melting range – above liquidus temperature T_s ;
2. range of the supercooled melt – between liquidus temperature T_s and transformation temperature T_g ;
3. frozen-in, quasi-solid melt (“glass range”), below transformation temperature T_g .

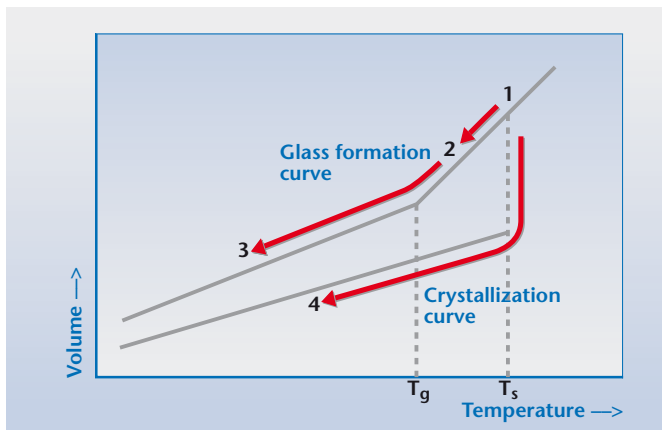


Fig. 8. Schematic volume–temperature curves for crystallization and glass formation:

1: liquid, 2: supercooled liquid, 3: glass, 4: crystal;

T_s : melting temperature, T_g : transformation temperature

The absence of any significant crystallization in the range of the supercooled melt (compare Figure 8 (2)) is of utmost importance for glass formation. Hence a basically steady and smooth change in the viscosity in all temperature regions is a fundamental characteristic of glass (Figure 9).

The temperature dependence of the viscosity (see Figure 10) is the crucial property for glass production.

Melting and fining (homogenization) must generally take place at viscosities ≤ 200 dPa·s; for glasses with low melting temperature, 1 dPa·s can be achieved.

Typical processing techniques for glasses, such as blowing, pressing, drawing and rolling, require viscosities in the range of 10^3 – 10^7 dPa·s. As a characteristic temperature for this “working range”, generally the temperature for 10^4 dPa·s, called the **working point** (ISO 7884-1), is measured and quoted (Table 12). Depending on the magnitude of the temperature interval between 10^3 dPa·s and 10^7 dPa·s, one distinguishes between “long” (large temperature difference, shallow slope) and “short” glasses.

At temperatures around the **softening point**, glass products deform rapidly under their own weight (forming by “sagging”), glass powders are sintered porously or densely, and glassblowing is carried out. The softening

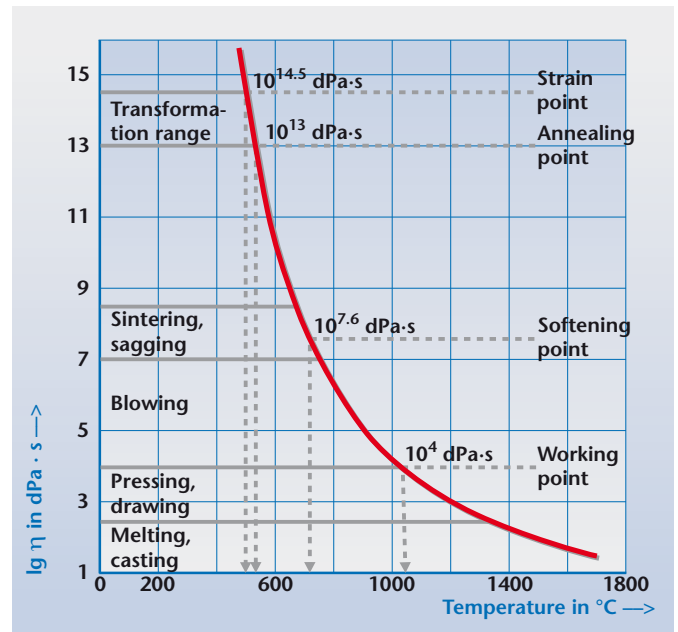


Fig. 9. Typical viscosity–temperature curve; viscosity ranges for important processing techniques and positions of fixed viscosity points

point is defined as the temperature at which the glass has a viscosity of $10^{7.6}$ dPa·s (method of measurement: ISO 7884-3).

Somewhat above 10^{10} dPa·s, the viscosity becomes increasingly time-dependent. With increasing viscosity (i.e.,

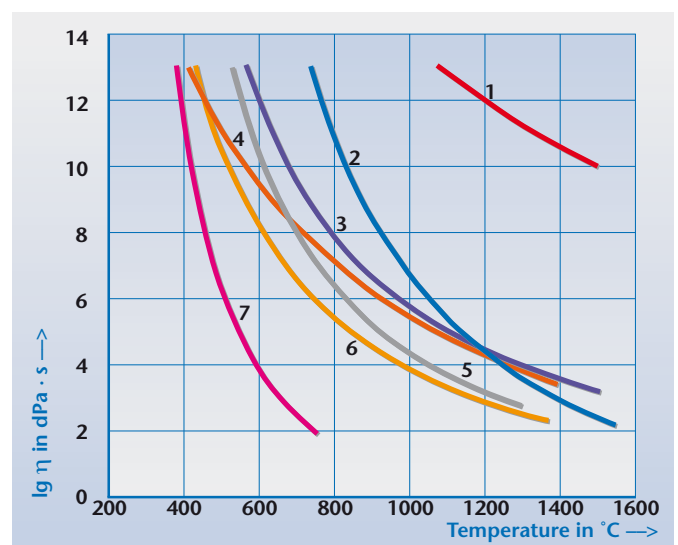


Fig. 10. Viscosity–temperature curves for some important technical glasses. 1: fused silica, 2: 8409, 3: 8330, 4: 8248, 5: 8350, 6: 8095, 7: 8465. Glasses with steep gradients (7) are called “short” glasses and those with relatively shallow gradients (4) are “long” glasses

decreasing temperature), the delay in establishing structural equilibria finally becomes so large that under normal cooling conditions the glass structure at 10^{13} dPa·s can be described as solidified or “frozen-in”. The low flow capability at this viscosity just suffices to compensate internal stresses in the glass after 15 min annealing time. On the other hand, the dimensional stability of the glass is sufficient for many purposes, and its brittleness (susceptibility to cracking) is almost fully developed. The glass is now in the transformation range, and many properties indicate this by changing the direction of their temperature dependence. Thus the change in the slope of the coefficient of linear expansion is used to define the transformation range by the so-called **transformation temperature** T_g according to ISO 7884-8 (Figure 17).

At this transformation temperature, most glasses show viscosities in the range of 10^{12} – $10^{13.5}$ dPa·s. The “ 10^{13} temperature”, at which the glass has a viscosity of 10^{13} dPa·s (method of measurement: ISO 7884-4), is called the **annealing point**. It is of crucial importance for stress relaxation after the hot forming of glasses, indicating the upper temperature limit of the so-called annealing range, at which internal stress is released within minutes. The lower limit of the annealing range is indicated by the **strain point**, at which the glass has a viscosity of $10^{14.5}$ dPa·s (determination: extrapolation from the viscosity-temperature curve). For most glasses, the strain point lies about 30–40 K below the annealing point. Relaxation of internal stresses here already takes 3–5 hours. Therefore faster cooling is possible at temperatures below the strain point without freezing in new stresses. On the other hand,

the strain point marks the maximum value for short-term heat load. Thermally prestressed glasses, in contrast, show significant stress relaxation already at 200–300 K below T_g . For glasses with precisely defined dimensions (e.g., etalons or gauge blocks) and in case of extreme demands on the stability of certain glass properties, application temperatures of 100–200 °C can already be the upper limit.

3.2 Strength

The high structural (= theoretical) strength of glasses and glass ceramics ($> 10^4$ MPa) can not be used in practice since the strength of glass articles is actually determined by surface defects induced by wear. Contact with hard materials often causes damages in the surfaces of glass and glass ceramic articles in the form of tiny chips and cracks, at whose tips critical stress concentrations may be induced by mechanical load, causing breakage of the articles.

In ductile materials such as metals, these stress concentrations are relieved by plastic flow. Glasses and glass ceramics, in contrast, behave as brittle as ceramics. At typical application-specific temperatures and load times, they show no plastic flow by which the stress concentrations at the chip and crack tips could be relieved.

Regarding strength, surface damages are therefore particularly important for glass and glass ceramic articles.

Surface Condition

As a result of wear-induced surface defects, glass and glass ceramic articles have practical tensile strengths of 20–200 MPa, depending on the surface condition

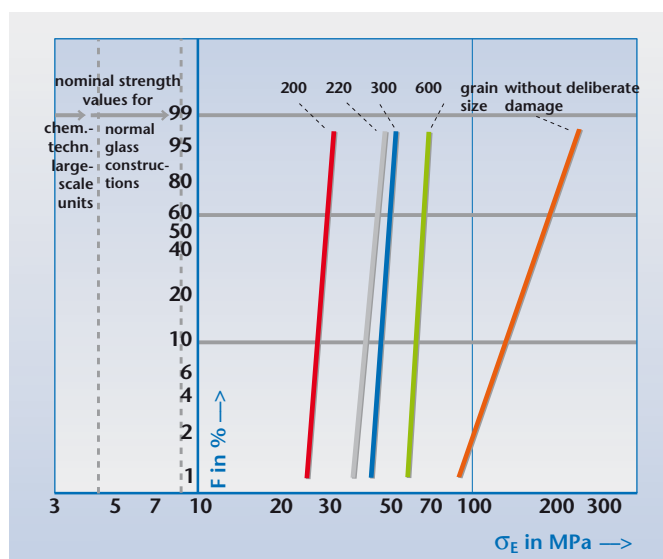


Fig. 11. Failure probability F for samples abraded by variously sized grains; predamaged surface area: 100 mm^2 , rate of stress increase $\sigma = 10 \text{ MPa} \cdot \text{s}$

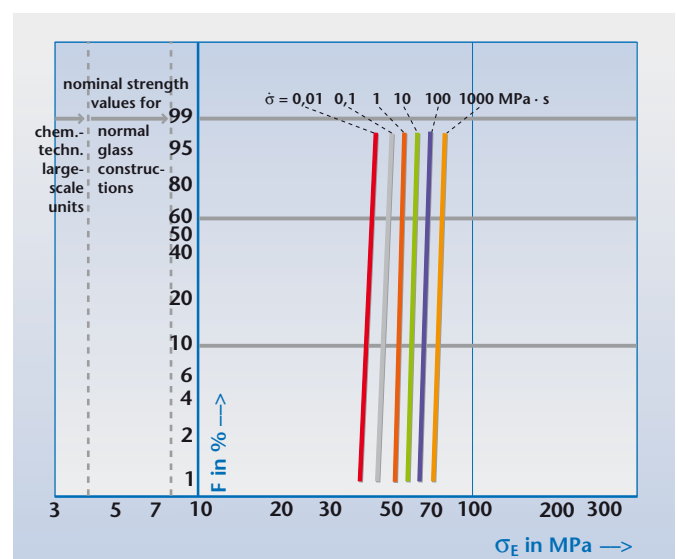


Fig. 12. Failure probability F of a predamaged surface for various rates of stress increase σ . (predamaged area: 100 mm^2 , grain size: 600)

(Figure 11) and exposure conditions. Only a slight – as a rule negligible – dependence on the chemical composition is found for silicate glasses.

Stress rate

In the testing and application of tensile strength values, the rate of stress increase and the size of the glass area exposed to maximum stress are particularly important. In contrast to the rapid stress increase occurring on impact, for example, slowly increasing tensile stress or continuous stress above certain critical limits may – as a result of stress corrosion cracking – cause the propagation of critical surface flaws and cracks and thus enhance their effect. Hence the tensile strength is time-dependent and stress rate-dependent (mainly important for test loads), as shown in Figure 12. Independent of surface damages or initial tensile strength, increasing the stress rate by a factor often results in an increase of strength of about 15%.

Constant loading

Fracture analyses of the cause and origin and behavior of cracks in glasses and glass ceramics yield further information about the relationship between the experimentally determined tensile strength σ_E (usually measured at rapidly increasing load) and the tensile strength σ_D expected under constant loading (= fatigue strength); see Figure 13. Such analyses show that, depending on the glass type, the tensile strength under constant loading, σ_D (for years of loading), will only amount to about 1/2 to 1/3 of the experimental tensile strength σ_E .

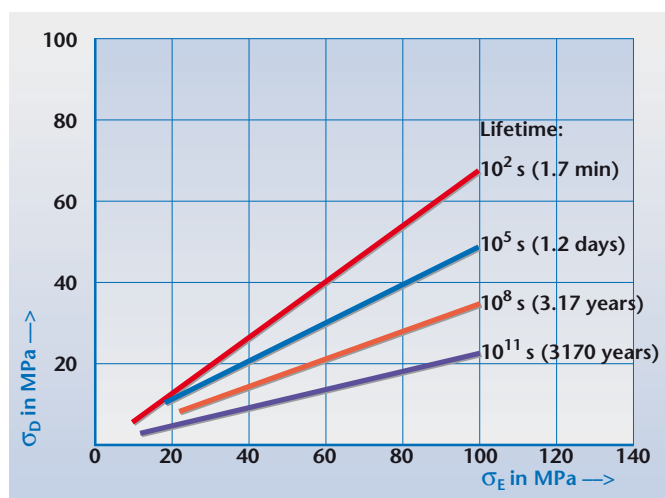


Fig. 13. Time-related strength σ_D (strength under constant loading) compared to experimental strength σ_E at $10 \text{ MPa} \cdot \text{s}$ stress increase with lifetime t_L , in normally humid atmosphere (soda-lime glass).

Area dependence

The larger the stressed area, the higher is the probability of large defects (large crack depths) within this area. This relationship is important for the transfer of experimental tensile strengths, which are mostly determined at relatively small test samples, to practical glass applications such as pipelines, where many square meters of glass can be uniformly stressed (Figure 14).

Strengthening

Surface defects, which are of decisive importance for tensile stresses, become ineffective in glasses subjected to compressive stress. The compressive strength of glasses is so high that it virtually sets no limits to technical applications of glass.

The high compressive strength of glass is exploited for strengthening by prestressing (also erroneously called toughening). Internal stresses are induced in glass articles with simple geometries – for example flat glass – which put the entire surface of the article under uniform compressive stress and result in a corresponding tensile stress in the interior of the glass.

Such internal stresses can be induced by rapid cooling (quenching) of the softened glass (Figure 15) or, in suitable glasses, by ion exchange in the approximately $50\text{--}200 \mu\text{m}$ thick surface layer. In subsequent external loading (tensile or bending), the externally induced stress adds to the internal stress. Up to the value of the compressive surface stress, a superimposed tensile stress keeps the surface under total compressive load. Thus, surface condition, loading rate, and loading time do not influence the strength.

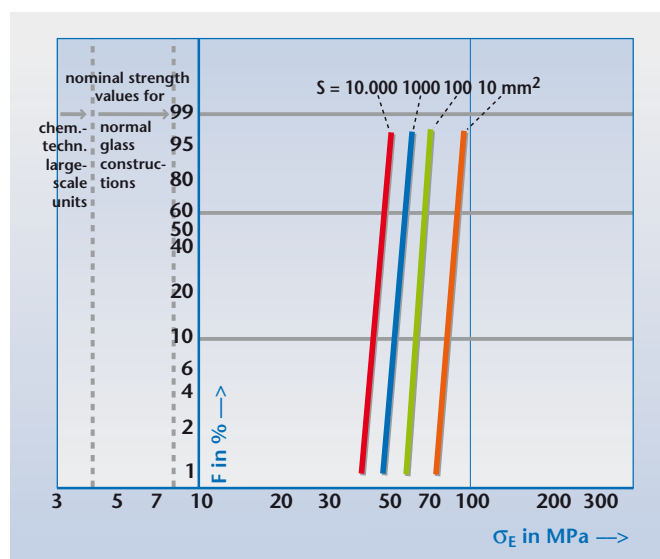


Fig. 14. Failure probability F for differently sized stressed areas S ; all samples abraded with 600 mesh grit, stress rate $\sigma = 10 \text{ MPa} \cdot \text{s}$

3.3 Elasticity

The ideal brittleness of glasses and glass ceramics is matched by an equally ideal elastic behavior up to breaking point. The elastic moduli for most technical glasses is within the range of 50–90 GPa. The mean value of 70 GPa is about equal to the Young's modulus of aluminum. The Poisson's ratio of most glasses is in the range 0.21 to 0.25 and is lower than for metals or plastics.

3.4 Coefficient of linear thermal expansion

With few exceptions, the length and the volume of glasses increase with increasing temperature (positive coefficient).

The typical curve begins with a zero gradient at absolute zero (Figure 16) and increases slowly. At about room temperature (section A), the curve shows a distinct bend and then gradually increases up to the beginning of the experimentally detectable plastic behavior (section B = quasi-linear region). A distinct bend in the extension curve characterizes the transition from the predominantly elastic to the more visco elastic behavior of the glass (section C = transformation range). As a result of increasing structural mobility, the temperature dependencies of almost all glass properties are distinctly changed. This transformation range is characterized by the transformation temperature T_g according to ISO 7884-8. Figure 17 shows the linear thermal expansion curves of five glasses; 8330 and 4210 roughly define the normal range of technical glasses, with expansion coefficients $\alpha_{(20^\circ\text{C}; 300^\circ\text{C})} = 3.3 - 12 \times 10^{-6}/\text{K}$. The linear thermal expansion is an essential variable for the sealability of glasses with other materials and for thermally induced stress formation, and is therefore of prime importance for glass applications.

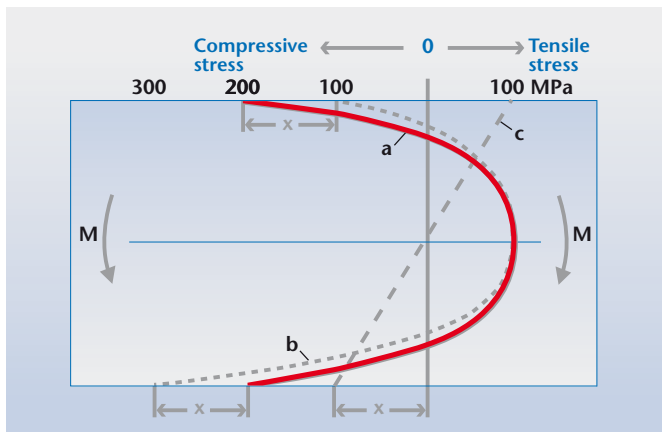


Fig. 15. Stress distribution across the thickness of thermally prestressed flat glass (a) without, (b) with additional bending M ; (c) stress distribution in bending without prestressing

Sealability

In fusion sealing with other materials, the decisive glass property is the linear contraction. As Figure 18 shows, the experimental setting point T_E lies in the already sharply bent section of the glass curve, and the experimental setting temperature increases with increasing cooling rate. Predicting the linear contraction is only possible if the shape of the glass curve and the setting point T_E for the respective cooling rate are known. The stress-optical measurement of stresses in test fusions with practice-oriented cooling rates (ISO 4790) is a simpler and much more accurate method of testing the sealability.

Thermal stresses

Owing to the low thermal conductivity of glass (typically $0.9 - 1.2 \text{ W}/(\text{m} \cdot \text{K})$ at 90°C , or a minimum of $0.6 \text{ W}/(\text{m} \cdot \text{K})$ for high-lead containing glasses), temperature changes produce relatively high temperature differences ΔT between the surface and the interior, which, depending on the elastic properties E (Young's modulus) and μ (Poisson's ratio), and on the coefficient of linear thermal expansion α , can result in stresses

$$\sigma = \frac{\Delta T \alpha E}{(1 - \mu)} [\text{MPa}].$$

In addition to the geometric factors (shape and wall thickness), the material properties α , E and μ decisively influence the thermal strength of glasses subjected to temperature variations and/or thermal shock. Thermal loads of similar articles made from different glasses are easily compared by means of the characteristic material value

$$\varphi = \frac{\sigma}{\Delta T} = \frac{\alpha E}{1 - \mu} [\text{MPaK}^{-1}],$$

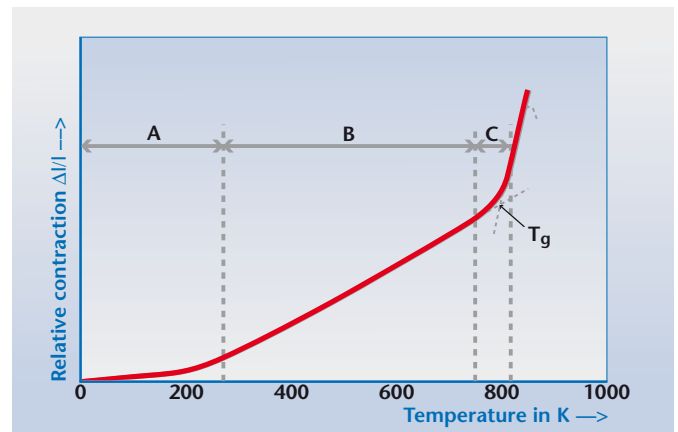


Fig. 16. Typical thermal expansion – temperature curve for glasses

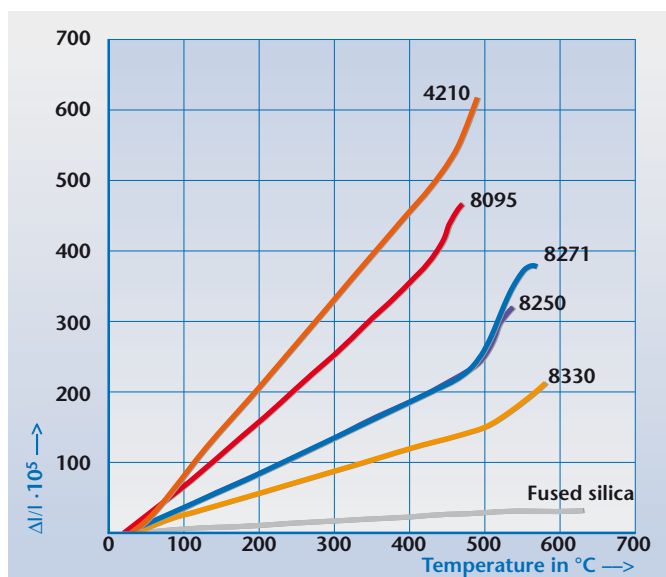


Fig. 17. Linear thermal expansion of various technical glasses and of fused silica

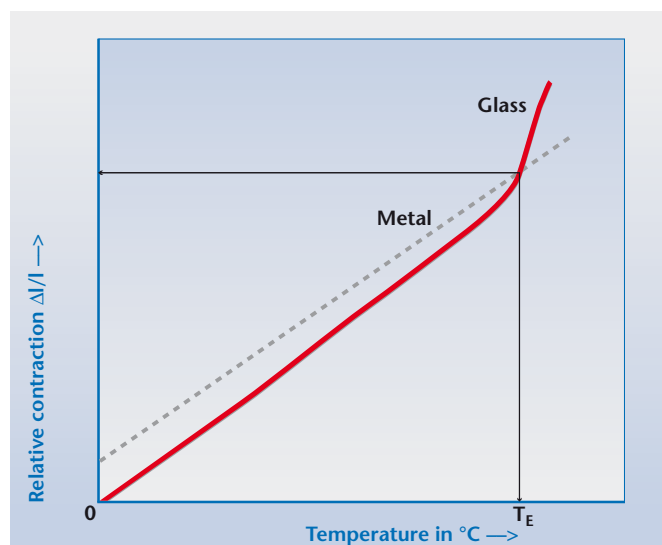


Fig. 18. Contraction/expansion curves of two fusion partners which are shifted so that they intersect at setting temperature T_E . The vertical difference thus describes the contraction difference with the correct sign

which indicates the maximum thermally induced stress to be expected in a flex-resistant piece of glass for a local temperature difference of 1 K. Because cracking originates almost exclusively from the glass surface and is caused

there by tensile stress alone, cooling processes are usually much more critical than the continuous rapid heating of glass articles.



Fig. 19. PYRAN® S fire resistant glazing resists fire without fracturing.

4. Electrical Properties



Fig. 20. Important for the functioning of the electronics: glass-to-metal components for airbags and seat belt tensioners

As electrically highly insulating materials, glasses are used in electrical engineering and electronics, for the production of high-vacuum tubes, lamps, electrode seals, hermetically encapsulated components, high-voltage insulators, etc. Moreover, glasses may be used as insulating substrates of electrically conducting surface layers (surface heating elements and data displays).

4.1 Volume resistivity

Electrical conductivity in technical silicate glasses is, in general, a result of the migration of ions – mostly alkali ions. At room temperature the mobility of these ions is usually so small that the volume resistivities with values above $10^{15} \Omega \text{ cm}$ are beyond the range of measurement. The ion mobility increases with increasing temperature. Besides number and nature of the charge carriers, structural effects of other components also influence the volume resistivity and its temperature relationship. The Rasch-Hinrichsen law applies to this relationship at temperatures below the transformation range:

$$\lg \rho = A - \frac{B}{T}$$

ρ = electrical volume resistivity
 A, B = specific glass constants
 T = absolute temperature.

The plot of $\log \rho = f(1/T)$ thus yields straight lines (Figure 21). Because of the relatively small gradient differences for most glasses, the electrical insulation of glasses is often defined only by the temperature for $10^8 \Omega \text{ cm}$. According to DIN 52326, this temperature is denoted as T_{k100} . The international convention is to quote volume resistivities for 250 °C and 350 °C, from which the constants A and B and various other values below T_g can be calculated.

4.2 Surface resistivity

The generally very high volume resistivities of glasses at room temperature are superposed in normal atmosphere by surface resistivities which are several orders of magnitude lower (Figure 22). The all-important factor is the adsorption of water at the glass surface. Depending on the glass composition, surface resistivities of 10^{13} – $10^{15} \Omega$ occur at low relative humidities, or 10^8 – $10^{10} \Omega$ at high

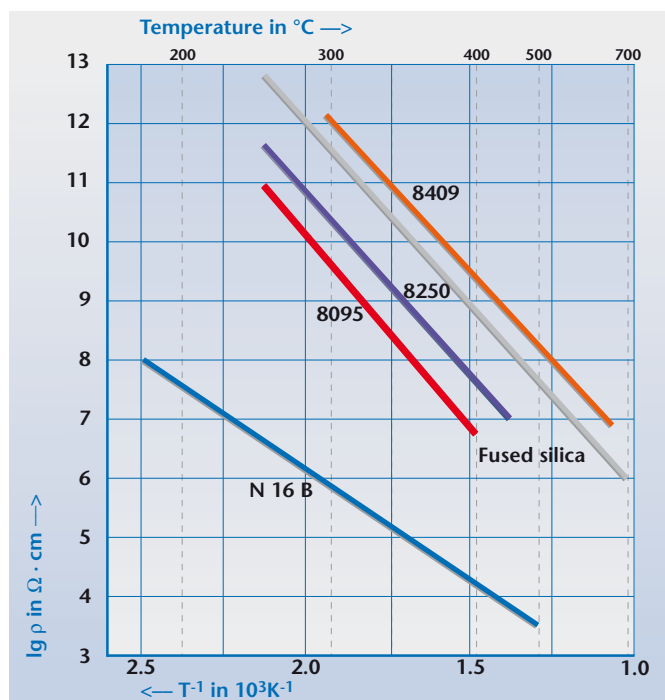


Fig. 21. Electrical volume resistivity of various technical glasses and fused silica related to the reciprocal of absolute temperature

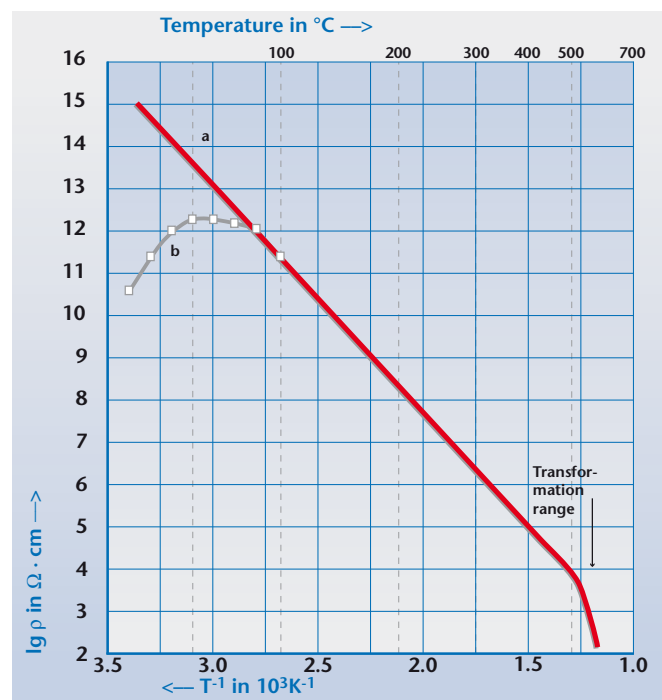


Fig. 22. Electrical resistance ρ of a soda-lime glass related to temperature (a) without, and (b) with hydrated layer

relative humidities. Above 100 °C, the effect of this hydrated layer disappears almost completely. Treatment with silicones also considerably reduces this effect.

Electrically conducting and transparent layers can be produced on glass by semi-conducting oxides (e.g., of tin and indium). The surface resistance range is 30–100 Ω.

4.3 Dielectric properties

The dielectric constant ϵ_r describes the relative increase in capacitance by introducing a polarizable dielectric into a condenser previously in vacuum. With dielectric constants generally between 4.5 and 8, technical glasses behave like other electrically insulating materials. Highest values are obtained for lead glasses such as 8531 ($\epsilon_r = 9.5$) and for ultra-high lead-containing solder glasses ($\epsilon_r = \sim 20$). The dependence of the dielectric constants ϵ_r on frequency and temperature is relatively small (Figure 23). For a frequency range of 50–10⁹ Hz, ϵ_r values will generally not vary by more than 10%.

Reversing the polarity and shifting the dipoles of a dielectric situated in an alternating electrical field will cause heating and hence dissipation as compared to ideal loss-free reactive power. The ratio of practical performance to ideal loss-free performance, which is dependent on the type of material as well as on frequency and temperature, is called the dielectric dissipation factor $\tan \delta$.

Due to the diverse mechanisms which cause such losses in glasses, there is a strong relationship to frequency, which shows minimum $\tan \delta$ values in the region of

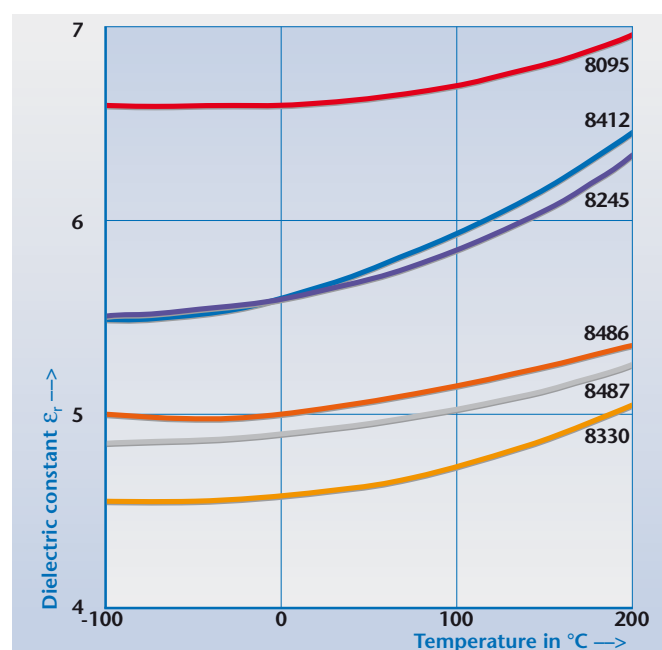


Fig. 23. Dielectric constant ϵ_r of electro-technical glasses related to temperature, measured at 1 MHz

10^6 – 10^8 Hz and increasing values for lower and higher frequencies (Figure 24).

At 10^6 Hz the dissipation factor $\tan\delta$ for different glasses lie between 10^{-2} – 10^{-3} ; fused silica, with 10^{-5} , has the lowest the dissipation factor of all glasses. The special glass 8248 has relatively low losses and $\tan\delta$ increases only slightly up to 5.5 GHz ($\tan\delta = 3 \times 10^{-3}$).

The steep increase in dielectric losses with increasing temperature (Figure 25) can lead to instability, i.e., to overheating of the glass due to dielectric loss energy in the case of restricted heat dissipation and corresponding electrical power.

4.4 Dielectric strength

Glasses that are free of inhomogeneities such as bubbles and impurities are dielectrically very stable and they often outperform porous electro-ceramics.

The dielectric strength of glasses depends on the frequency, the rate of increase in voltage, the temperature, the glass composition, and the external test conditions. Furthermore, the breakdown field strength increases substantially with decreasing glass thickness, indicating heat breakdown (interrelated increase in temperature and electrical conductivity) as the preferred breakdown mechanism. "Cold" breakdown caused by the sudden formation of an electron avalanche is technically unimportant.

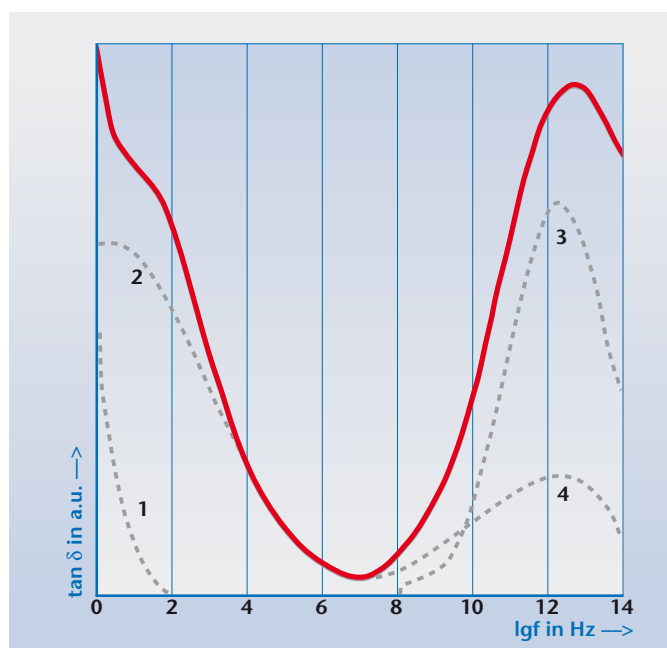


Fig. 24. Schematic representation of the frequency spectrum of dielectric losses in glass at room temperature (Stevens). The solid curve gives the total losses built-up from: 1. conduction losses, 2. relaxation losses, 3. vibration losses, and 4. deformation losses

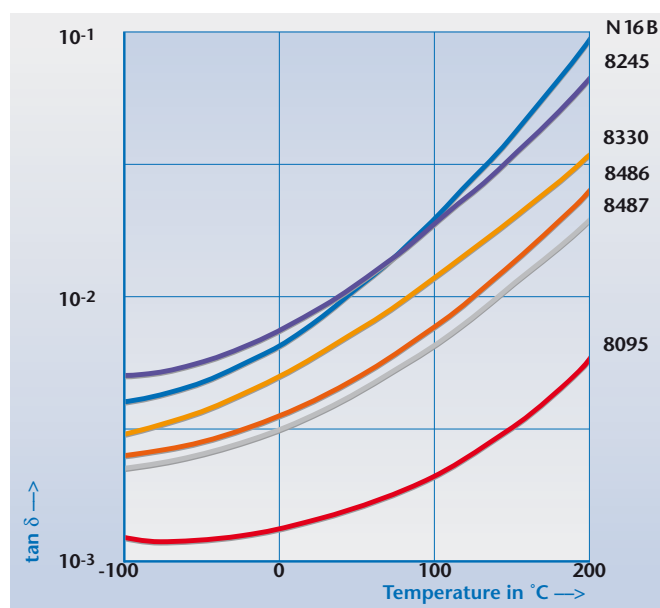


Fig. 25. Dissipation factor $\tan\delta$ as a function of temperature in the range -100 to $+200$ °C, measured at 1 MHz

Approximate values for the dielectric strength of glass are field strengths of 20–40 kV/mm for glass thicknesses of 1 mm at 50 Hz at 20 °C, and 10–20 kV/mm for greater thicknesses. At higher temperatures and frequencies, decreasing values can be expected.



Fig. 26. Close-up of the front of an ozonizer, inside

5. Optical Properties



Fig. 27. Synthesis of form and function

5.1 Refraction of light

The ratio of the speed of light in vacuum to that in a defined material is called the refractive index n_λ of that material. The refractive index of glasses is dependent on the wavelength (dispersion). This is a decisive factor in purely optical applications.

The refractive indices n_d of technical glasses are valid for $\lambda_d = 587.6 \text{ nm}$ and generally lie within the range of 1.47–1.57. Exceptions to this rule are lead glasses with PbO contents of over 35% (8531 : $n_d = 1.7$). The principal dispersion $n_F - n_C$ ($\lambda_F = 486.1 \text{ nm}$, $\lambda_C = 656.3 \text{ nm}$) of technical glasses lies between 0.007 bis 0.013.

At the boundary glass surface–air, the incident light is partly reflected. At perpendicular incidence, the reflectance R_d (wavelength $\lambda_d = 587.6 \text{ nm}$) is calculated by

$$R_d = \left(\frac{n_d - 1}{n_d + 1} \right)^2$$

to be 3.6% to 4.9% per interface.

The transmittance τ_d and the reflectance ρ_d of a non-absorbing plane-parallel glass plate with two glass-air surfaces, with multiple reflections taken into account, are given by

$$\tau_d = \frac{(1 - R_d)^2}{1 - R_d^2} = \frac{1 - R_d}{1 + R_d} = \frac{2n_d}{n_d^2 + 1}$$

and

$$\rho_d = \frac{2R_d}{1 + R_d} = \frac{(n_d - 1)^2}{n_d^2 + 1}.$$

The transmittance τ_g at perpendicular incidence decreases correspondingly to values between 93.1% and 90.6%.

Reflection (particularly in the case of oblique incident light) can considerably disturb or even eliminate the transparency of glass. Therefore, in stress-optical testing for example, it is often necessary to immerse the sample in liquids of the same refractive index.

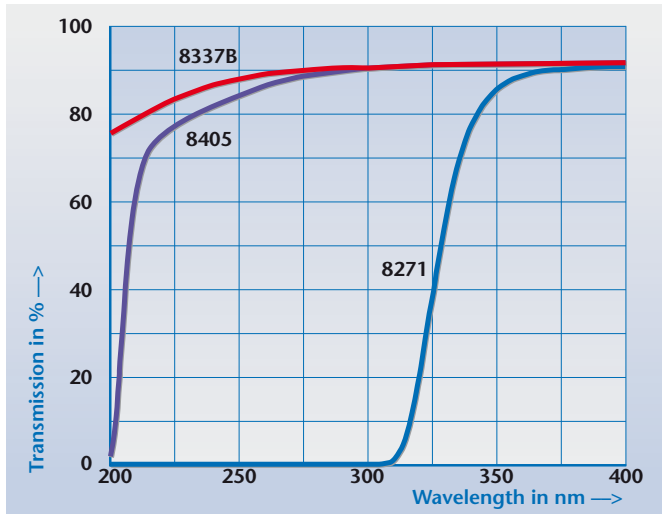


Fig. 28. UV-transmission of highly UV-transparent technical glass types 8271, 8337B and 8405 at 0,5 mm glass thickness

5.2 Stress birefringence

Owing to its very structure, glass is an isotropic material. Mechanical stress causes anisotropy which manifests itself as stress-induced birefringence. A ray of light impinging on glass will be resolved into two components vibrating in planes perpendicular to each other and having different phase velocities. After passing through a plate of thickness d which is subjected to a principal stress difference $\Delta\sigma$, there exists an optical path difference Δs between the two components. This path difference can either be estimated by means of the birefringence colors or measured with compensators:

$$\Delta s = K d \Delta\sigma [\text{nm}].$$

K is the stress-optical coefficient of the glass (determination according to DIN 52314).

$$K = \frac{\Delta s}{d} \frac{1}{\Delta\sigma} [\text{MPa}^{-1}]$$

Many glasses have stress-optical coefficients of about $3 \times 10^{-6} \text{ MPa}^{-1}$, and borosilicate glasses of up to $4 \times 10^{-6} \text{ MPa}^{-1}$. High-lead-content glasses can have values down to nil or even negative.

Stress-optical measurements permit the determination of permanent stress in glass (state of annealing) as well as of reactive stress caused as a reaction to exterior forces. Stress-optical measurements for the evaluation of glass seals with other glasses, metals, or ceramics are of particular importance. These offer a sensitive method of determining thermal expansion and contraction differences.

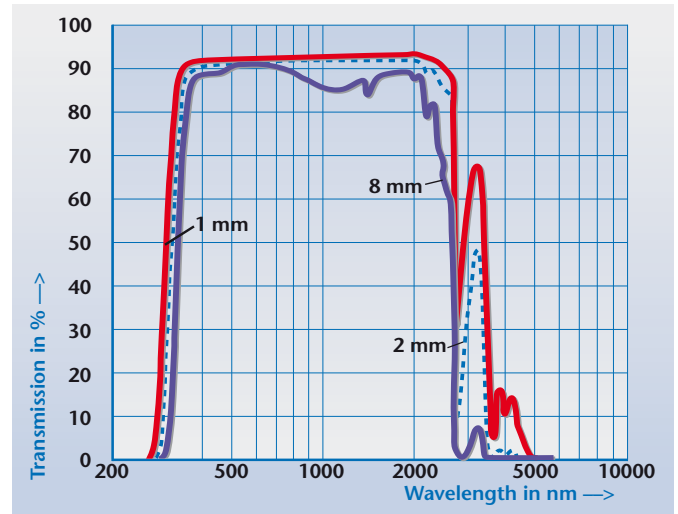


Fig. 29. Transmission of DURAN® 8330 for thicknesses 1, 2 and 8 mm

5.3 Light transmittance

Normally, glass is transparent to visible light. Losses occur primarily due to reflection, as indicated above. This transparency can be reduced by coloring agents (oxides of transition elements or colloids, coloured glasses) or by fine particles in the glass, which have different refractive indices (light dispersion, opal glasses).

Absorption caused by impurities such as Fe_2O_3 or by major components such as PbO strongly reduce transparency in the UV range. The best UV transmission is achieved by pure fused silica (UV cut-off for 1 mm thickness is in the region of 160–180 nm); particularly good UV-transmitting multi-component glasses have cut-offs of up to 220 nm wavelength (Figure 28); normal technical glasses (Figure 29) already absorb considerably at 300 nm.

6. Chemically Highly Resistant Glasses

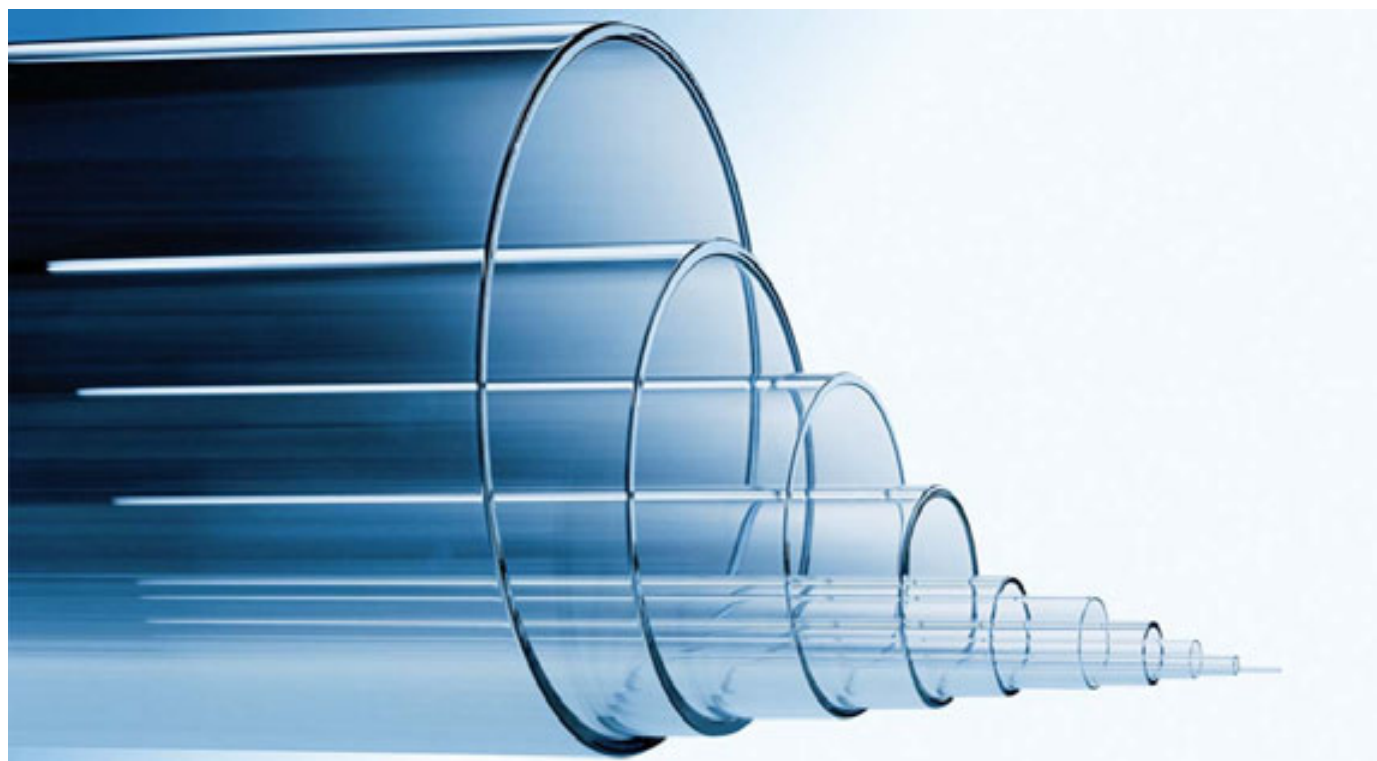


Fig. 30. DURAN® tubing for a wide range of applications

The chemically resistant glasses categorized as “borosilicate glasses” contain a high percentage of silica (70–80%), considerable amounts of boric oxide (7–13%), as well as alkali oxides (Na_2O , K_2O , 4–8%), alumina (2–7%), and sometimes alkaline-earth oxides (CaO , BaO , 0–5%). Characteristically, they have high chemical durability (hydrolytic class 1, acid class 1) and relatively low thermal expansion, giving high thermal resistance and enabling the manufacture of large, thick-walled components from these glasses.

These exceptional properties of borosilicate glasses were recognized by Otto Schott, and large-scale melts were first put to use in 1892.

Chemically durable borosilicate glasses have such a high acid resistance that even for surface areas as large as 400 cm^2 , exposed to a six-hour boiling in 20% hydrochloric acid, only very small weight losses can be measured. Because the measurement accuracy in determining the variation in weight of glasses having large surface areas is roughly equivalent with the weight losses themselves, a sound comparison between the different glasses of this group is impossible. The values simply indicate high acid resistance.

On the other hand, silicate glasses with higher boric oxide contents (>15%) are generally not classified as chemically resistant. Examples are electro-technical sealing glasses such as 8245 or 8250, which fall into acid class 4 and 3, respectively.

6.1 DURAN®

The coefficient of linear thermal expansion of $3.3 \times 10^{-6}/\text{K}$ is the lowest of all the large-scale mass-produced technical glasses with high chemical resistance. The low specific thermal stress $\varphi = 0.24\text{ N}/(\text{mm}^2\text{ K})$ indicates its exceptional resistance to thermal shock and temperature variations. These properties allow the production and hot forming of large, thick-walled articles which can be exposed to application temperatures of up to max. 200°C .

Its thermal properties coupled with outstanding water and acid resistance, make DURAN® a highly suitable material for application in laboratories and large-scale chemical plants, for example as pipelines, reaction vessels, heat exchangers, and so on.

For thin-walled DURAN® items, application temperatures can lie considerably above 200°C . To guarantee shape stability, a maximum of 500°C should not be exceeded.

DURAN® is made into tubes of up to 450 mm in diameter and into pressed and blown glassware. Processed as flat glass, it is available as a floated product under the tradename BOROFLOAT® 33 and as a rolled sheet glass under the tradename SUPREMAX® 33 for applications in home appliances, lighting, chemical engineering, safety, optics, precision engineering and photovoltaics. Figures 31 and 33 illustrate the chemical resistance.

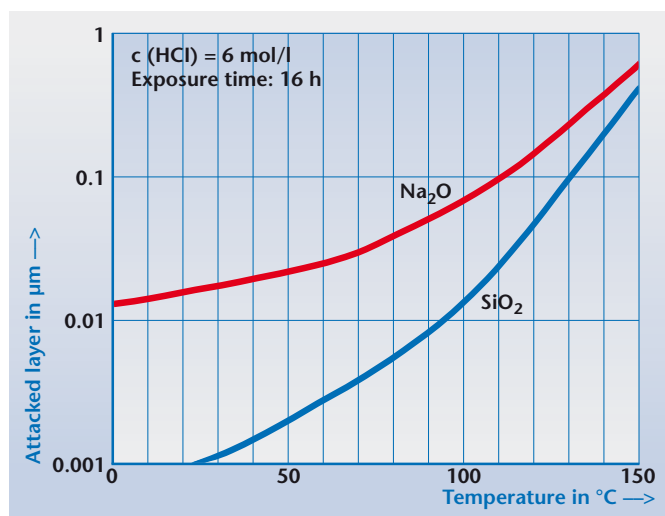


Fig. 31. Acid attack on DURAN®/BOROFLOAT® 33/SUPREMAX® 33 8330 as a function of temperature and calculated from leached amounts of Na₂O and SiO₂

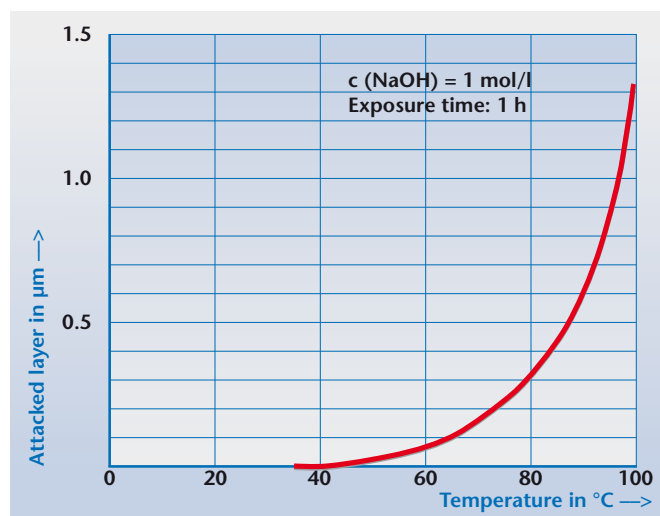


Fig. 33. Alkali attack on DURAN®/BOROFLOAT® 33/SUPREMAX® 33 8330 as a function of temperature and calculated from the weight losses

6.2 SCHOTT SUPRAX® 8488

With thermal expansions of $4.1 \times 10^{-6}/\text{K}$ and $4.3 \times 10^{-6}/\text{K}$, SUPRAX® glasses have characteristically lower melting and working temperatures as a result of smaller amounts of SiO₂ and B₂O₃ in favor of alkali and alkaline-earth oxides, as com-

pared to DURAN®. With specific thermal stresses $\varphi = 0.34$ or $0.36 \text{ N}/(\text{mm}^2 \text{ K})$, SUPRAX® glasses are also classified as thermally resistant and are manufactured into articles of medium wall thickness which can be thermally stressed.

SUPRAX® 8488 has increased alkali resistance and its thermal expansion of $4.3 \times 10^{-6}/\text{K}$ already allows sufficient thermal prestressing.



Fig. 32. Syringes made from FIOLAX® neutral glass tubes

6.3 SCHOTT FIOLAX®

These highly resistant borosilicate glasses are particularly suited for pharmaceutical parenteral packaging such as syringes, ampoules and vials for high-grade injection solutions. Their manufacturing, exclusively in the form of tubes, is today possible with exceptionally tight diameter and wall thickness tolerances. Therefore, the production of syringes, ampoules and vials and their filling on the high-speed filling lines of the pharmaceutical industry are unproblematic. Because the wall thickness of the tubes is comparatively small, thermal stresses in subsequent processing are not critical, despite thermal expansions of $4.9 \times 10^{-6}/\text{K}$ and $5.4 \times 10^{-6}/\text{K}$, respectively.

FIOLAX® tubes guarantee highest quality and outstanding chemical stability. Containers made from these glasses, sometimes also called “neutral glasses”, fulfil all the specifications given in the European Pharmacopoeia and in the various pharmacopoeia of other nations.

SCHOTT FIOLAX® clear, 8412

This glass belongs to the chemically resistant alkaline earth containing borosilicate glass type. Its water and acid resistance, correspond to those of DURAN®, and its alkali resistance is even higher. Alkaline preparations up to pH values of 12 can be stored and autoclaved in FIOLAX® clear.

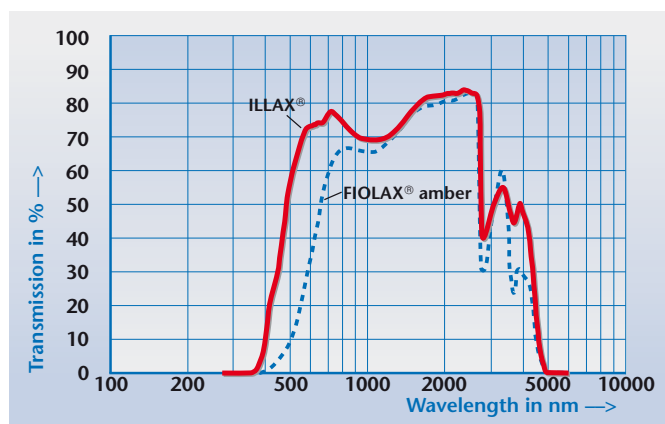


Fig. 34. Spectral transmittance of FIOLAX® amber and ILLAX® for 1 mm glass thickness

SCHOTT FIOLAX® amber, 8414

Due to additions of iron and titanium oxides, this borosilicate glass exhibits high light absorption in the blue and UV spectral regions. Sensitive pharmaceutical preparations can therefore be effectively protected from light in the critical wavelength region.

6.4 SCHOTT BOROFLOAT® 33/ SCHOTT SUPREMAX® 33

BOROFLOAT® 33 and SUPREMAX® 33 are both high quality borosilicate glasses with impressive properties that make them suitable for a wide range of applications. BOROFLOAT® 33 is manufactured using the Microfloat process, whereas SUPREMAX® 33 is a rolled sheet glass produced using the unique SCHOTT rolled glass method.

The chemical composition of BOROFLOAT® 33/SUPREMAX® 33 complies with the requirements for a typical borosilicate glass to DIN ISO 3585 and EN 1748 Pt. 1

Table 4. Values of chemical stability

Glass type	Hydrolytic resistance DIN ISO 719 Consumption of 0.01 mol/l HCl ml/g glass	Hydrolytic resistance DIN ISO 720 Consumption of 0.02 mol/l H ₂ SO ₄ ml/g glass	Acid resistance DIN 12 116 Weight loss mg/dm ²	Alkali resistance DIN ISO 695 Weight loss mg/dm ²
DURAN®/BOROFLOAT® 33/SUPREMAX® 33 8330	0.030	0.02	0.4	136
SUPRAX® 8488	0.029	0.03	0.3*	92
FIOLAX® clear 8412	0.030	0.04	0.4	110
FIOLAX® amber 8414	0.030	0.04	0.6	115
PYRAN® S 8341	0.033	n.n.	0.3	130

* DIN ISO 1776



Fig. 35. BOROFLOAT® 33 is a highly versatile high-tech material suitable for manifold applications in industry, engineering, architecture, art, and science and research

respectively. Like all borosilicate glasses BOROFLOAT® 33/SUPREMAX® 33 demonstrates a high resistance to water, many alkalis and acids as well as organic substances. Its chemical resistance is superior to that of most metals even in long-term use and at temperatures in excess of 100 °C (as used as sight glasses in the chemical industry). Exposure to water and acids only results in the leaching out of small amounts of ions from the glass (as used in medicine and analytical engineering).

BOROFLOAT® 33/SUPREMAX® 33 consists of natural raw materials and is harmless to human beings and the environment. It is in accordance to the requirements of the European guideline ROHS/2002/95. The glass can be recycled for further use.

7. Sealing Glasses

7.1 General

Glasses are best suited for the production of mechanically reliable and vacuum-tight fusion seals with metals and ceramics. Particularly favoured properties are the viscosity behaviour of glass and the direct wettability of many crystalline materials by glasses.

A necessary condition for the stability and mechanical strength of glass seals is the limitation of mechanical stress in the glass component for temperatures encountered during production and use. To ensure “sealability” (which means that the thermal contractions of the two sealing components match each other below the transformation temperature of the glass), often glasses of a special composition, so-called sealing glasses, are developed. Apart from sealability, such glasses must very often fulfil other requirements such as high electrical insulation, special optical properties, etc. The sealability can be tested and evaluated with sufficient accuracy and certainty by stress-optical measurements in the glass portion of a test seal (ISO 4790).

Apart from characteristic material values such as coefficient of linear thermal expansion, transformation temperature, and elastic properties, also the cooling rate (Figure 37) and the shape can have considerable influence on the degree and distribution of seal stresses.



Fig. 36. Reed switches encapsulated in SCHOTT glass type 8516

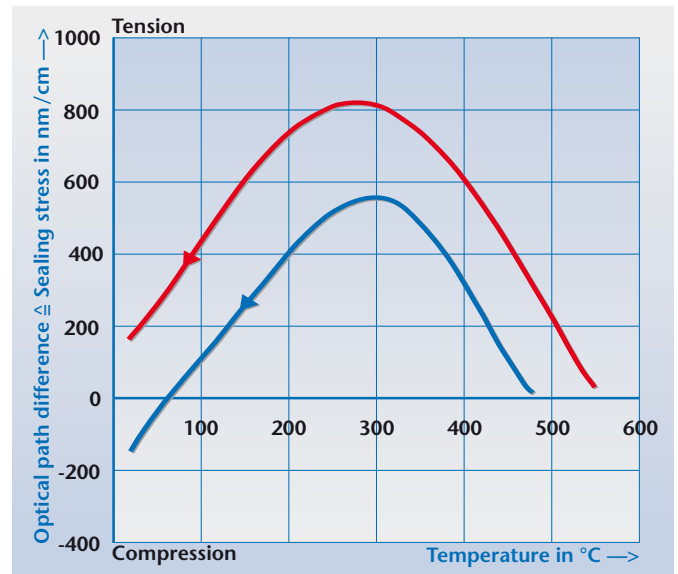


Fig. 37. Influence of cooling rate on the temperature–sealing stress relationship in a 8516–52 Ni/Fe combination; blue curve: low cooling rate, red curve: high cooling rate

7.2 Types of sealing glasses

In reference to the expansion coefficients of technically applied sealing metals (e.g. tungsten and molybdenum) and alloys (of Ni-Fe-Co, Ni-Fe-Cr, and other special materials), the corresponding sealing glasses are grouped and designated as “tungsten sealing glasses”, “Kovar glasses”, etc. (see table 5).

Alkaline-earth borosilicate glasses (8412) and aluminosilicate glasses (8252, 8253) have the necessary sealability and thermal resistance to be particularly suitable for tungsten and molybdenum sealings frequently used in heavy-duty lamps.

Tungsten is very often used as a metal wire for highly developed and highly stressed seals. For this, a group of glass types with different further properties are available (8487).

Table 5. Special properties and principal applications of technically important sealing glasses, arranged according to their respective sealing partners

Metal ($\alpha_{20/300}$ in $10^{-6}/K$)	Glass-number	Glass characteristics	Main applications
Tungsten (4.4)	8337B	borosilicate glass, highly UV-transmitting	photomultiplier, UV-detectors
	8487	high boron content, low melting temperature	flash lamps, lamp bulbs, exhaust and flare tubes, discharge lamps
Molybdenum (5.2)	8412	alkaline-earth borosilicate, high chemical resistance Fiolax® clear	pharmaceutical packaging
	8252	alkaline-earth alumino-silicate glass, free from alkali	halogen lamps
	8253	alkaline-earth alumino-silicate glass, free from alkali, high temperature resistance	halogen lamps
Molybdenum and 28 Ni/18 Co/Fe (5.1)	8245	high boron content, low melting temperature, low x-ray absorption	x-ray tubes, photomultiplier
	8250	high boron content, low melting temperature, high electric insulation, low dielectric losses	transmitting tubes, image converters clad tubes for optical fibres, x-ray tubes, glass-to-metal seal packages
	8271	borosilicate glasses, high UV-blocked, stabilised against solarisation	backlights
28 Ni/23 Co/Fe (7.7)	8436	alkali alkaline-earth silicate, sealable with sapphire, resistant to Na vapor and alkalis	
51 Ni/1Cr/Fe (10.2)	8350	soda-lime silicate glass, AR-Glas®	
Cu-sheathed ($\alpha_{20/400}$ radial 99) ($\alpha_{20/400}$ axial 72)	8531	dense-lead silicate, Na- and Li-free, low melting temp., high electrical insulation	low-temperature encapsulation of diodes
	8532		
	8360		
52 – 53 Ni/Fe (10.2. – 10.5.)	8516	containing FeO for hot forming by IR, low volatilization, lead-free	reed switches

Ni-Fe-Co (Kovar) alloys are of great importance as substitutes for molybdenum. Suitable glasses (8245 and 8250) characteristically contain relatively high amounts of B₂O₃. These glasses have additional special properties, such as high electrical insulation, low dielectric loss and low X-ray absorption, and meet the most stringent requirements for vacuum tube technology and electronic applications. 8271 is a new glass type of this group and optimized for backlight applications.

For Ni-Fe-(Cr) alloys, which are frequently used in technical applications, as well as for copper-sheathed wire, glass groups belonging to the soft glass category are recommended. Such glasses usually meet certain special requirements, such as high electrical insulation (alkali-lead silicate 8095), exceptionally low working temperature (dense-lead glasses 8531, 8532), etc.

FeO-containing glass (8516) is frequently used for hermetic encapsulation of electrical switches and electronic components in inert gas. Hot forming and sealing are easily achieved by absorption of IR radiation having its maximum intensity at 1.1 μm wavelength (Figure 39). The presence of a portion of Fe₂O₃ makes these glasses appear green. At appropriately high IR intensities, they require considerably shorter processing times than flame-heated clear glasses.

7.3 Compression seals

A common feature of all compression seals is that the coefficient of thermal expansion of the external metal part is considerably higher than the thermal expansion

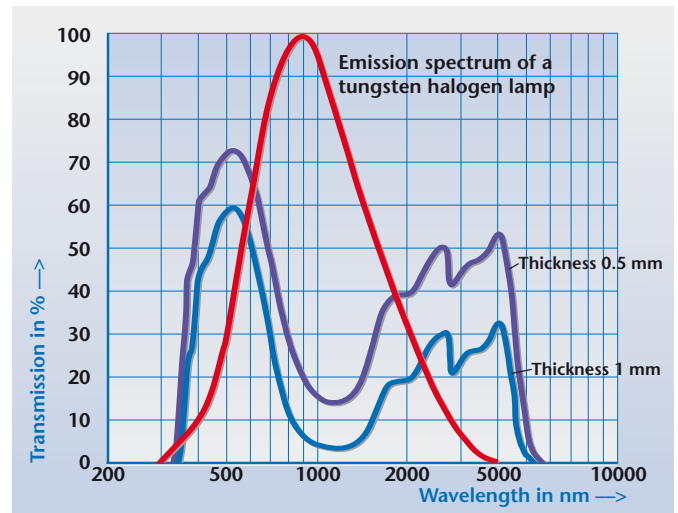


Fig. 39. IR absorption of Fe-doped glasses compared to the emission of halogen lamps. Transmission of reed glass 8516, thicknesses 0.5 mm and 1 mm, and emission of a tungsten halogen lamp (3000 K, rel. unit)

coefficients of the sealing glass and the metallic inner conductors. As a result, the glass body is under overall radial pressure after the sealing. This prestressing protects the glass body against dangerous mechanical loads and guarantees robust, mechanically insensitive seals. Because the compressive stress of the glass is compensated by a tensile stress in the jacket, the jacket wall must be sufficiently thick (at least 0.5 mm even for small seals) in order to be able to absorb such tensions permanently. Like adapted seals, compression seals can be produced as hard glass or soft glass seals. If the difference of the thermal expansion of the metallic jacket and the sealing glass is significantly higher than 5 ppm/K, an additional prestressing of the glass body results ("reinforced compression seal"); see Figure 40.

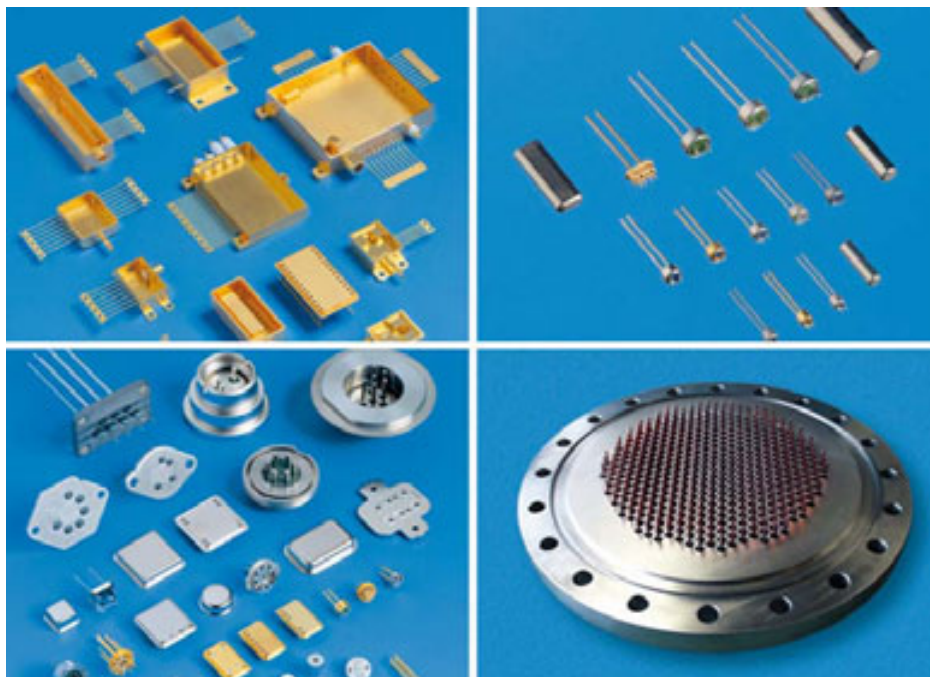


Fig. 38. Glass-to-metal feedthroughs

7.4 Ceramic glass seals

Dielectrically superior and highly insulating ceramics such as hard porcelain, steatite, Al_2O_3 ceramics, and forsterite exhaust almost the complete expansion range offered by technical glasses. Hard porcelain can generally be sealed with alkaline-earth borosilicate glasses, which are also compatible with tungsten. Glass seals with Al_2O_3 ceramics and steatite are possible with special glasses such as 8436, which will also seal with 28 Ni/18 Co/Fe alloy. Soft glasses with thermal expansions around $9 \times 10^{-6}/\text{K}$ are suitable for sealing to forsterite.

Ceramic seals that need to be free of alkalines and used for high temperature applications, can be achieved with the following glasses (s. table 6)

G018-266, G018-302, G018-337, G018-338 or G018-346 for Al_2O_3 -ceramics G018-339, G018-340 or G018-345 for ZrO_2 -ceramics

G018-266 and G018-338 are stable sealing glasses, whereas the other glasses in table 6 are crystallizing glasses, which have higher maximum application temperatures.

The glasses G018-337 to G018-340 are suitable for laser sealing processes:

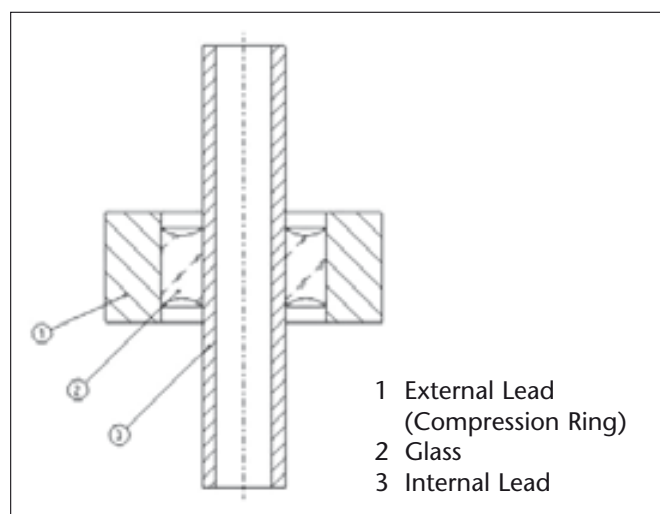


Fig. 40. Schematic of a typical compression seal

Table 6. Sealing glasses for high temperature applications

Glass No.	$\alpha_{(20/300)} [10^{-6} \text{ 1K}]$ glassy	$\alpha_{(20/300)} [10^{-6} \text{ 1K}]$ crystallized	T _g [°C]	Sealing temperature	T _c [°C]
G018-266	6,9	–	585	780	–
G018-302	5,7	–	887	1450	–
G018-337	8,1	10,2	662	1000	835
G018-338	7,5	–	673	1100	–
G018-339	9,8	10,6	627	990	767
G018-340	10,1	10,1	602	850	800
G018-345	10,3	–	598	830	–
G018-346	7,29	–	720	1270	800

T_c = peak crystallization temperature

7.5 Intermediate sealing glasses

Glasses whose thermal expansion differs so widely from that of the partner component that direct sealing is impossible for stress reasons must be sealed with intermediate sealing glasses. These glasses are designed for the recommended seal transitions in such a way that the sealing stresses do not exceed 20 N/mm² at room temperature.

Table 7. Sealing and intermediate sealing glasses

Glass No.	Sealing partners	$\alpha_{20/300}$	Transformation- temperature [°C]	Temperature at viscosities of			Density [g/cm ³]	t_{k100} [°C]
		[10 ⁻⁶ /K]		10 ¹³ dPa · s [°C]	10 ^{7.6} dPa · s [°C]	10 ⁴ dPa · s [°C]		
8228	Fused silica–8228–8229	1.3	~700	726	1200	1705	2.15	355
8229	8228–8229–8230	2.0	630	637	930	1480	2.17	350
8230	8229–8230–8330	2.7	570	592	915	1520	2.19	257
8447	8412–8447–Vacon 10	4.8	480	505	720	1035	2.27	271
8448	8330–8448–8449, 8486, 8487	3.7	510	560	800	1205	2.25	263
8449	8486 } –8449– 8412 8487 } 8447	4.5	535	550	785	1150	2.29	348
8450	8412–8450–KER 220 8436	5.4	570	575	778	1130	2.44	200
8454	KER 221 } –8454–Vacon 70 Al ₂ O ₃ }	6.4	565	575	750	1070	2.49	210
8455	8436 –8455–8456 8454	6.7	565	–	740	1030	2.44	–
8456	8455–8456–8350	7.4	445	–	685	1145	2.49	–

Note: type designation of the ceramics to DIN 40685; manufacturer of Vacon-alloys: Vacuumschmelze Hanau (VAC)

Table 8. Expansion coefficients of common material combinations for compression glass-to-metal seals

Designation	$\alpha_{(20/300)} [10^{-6} \text{ K}^{-1}]$		
	Compression Ring	Glass	Interior Lead
Standard compression glass-to-metal seals	13	9	9
Low-expansion standard compression glass-to-metal seals	9	5	5
Reinforced compression glass-to-metal seals	18	9	9
	13	5–7	5

Table 9. Sealing glasses for compression seals

Glass No.	Main applications	$\alpha_{(20/300)}$	Transformation temperature T_g [°C]	Glass temperatures in °C at viscosities dPas		Density [g/cm ³]	tk100 [°C]	log of the electric volume-resistivity in $\Omega \text{ cm}$ at		Dielectric properties at 25 °C for 1 MHz		Chemical resistance classes		
		[10 ⁻⁶ 1K]		10 ^{7,6}	10 ⁴			250 °C	350 °C	DZ	tan δ [10 ⁻⁴]	W	S	L
8350	Compression seals Seals with steels and NiFe alloys	9.0	520	708	1035	2.52	198	7.1	5.7	7.2	70	3	1	2
8421	Compression seals Seals with steels and NiFe alloys	9.6	525	721	1000	2.59	253	8.1	6.4	7.4	43	3	3	2
8422	Compression seals Seals with steels and NiFe alloys	8.6	540	722	1027	2.46	212	7.3	5.8	7.3	60	2	3	3
8629	Compression seals Seals with steels and NiCo 2918	7.6	529	720	1020	2.52	267	8.3	6.7	6.4	26	1	3	2
8630	Compression seals Seals with steels and NiFe alloys, increased requirements for electrolytic resistance and temperature stability	9.1	440	660	975	2.53	317	9.3	7.6	6.5	21	3	1/2	2

7.6 Glass and Glass Ceramic Sealants for Solid Oxide Fuel Cells (SOFC)

SOFC sealing materials are specially formulated glasses and glass ceramics that withstand the harsh environments and high operating temperatures of SOFCs. For the secure and stable combination of multiple cells into a high-performance cell-stack, the metallic layers that serve as interconnects between the individual cells require hermetic protection. Sealing glasses are applied in the form of a paste made of glass powder and an organic binding agent and are dispensed along the critical areas to the interconnects.

Besides providing hermetic sealing for the interconnects to prevent fuel-oxidant mixing, the sealings also serve as electrical insulation with a high electrical resistance at operating temperatures. Moreover, they feature chemical stability under reducing and oxidizing atmospheres and have a matched coefficient of thermal expansion (CTE) to prevent material stress within the structure.

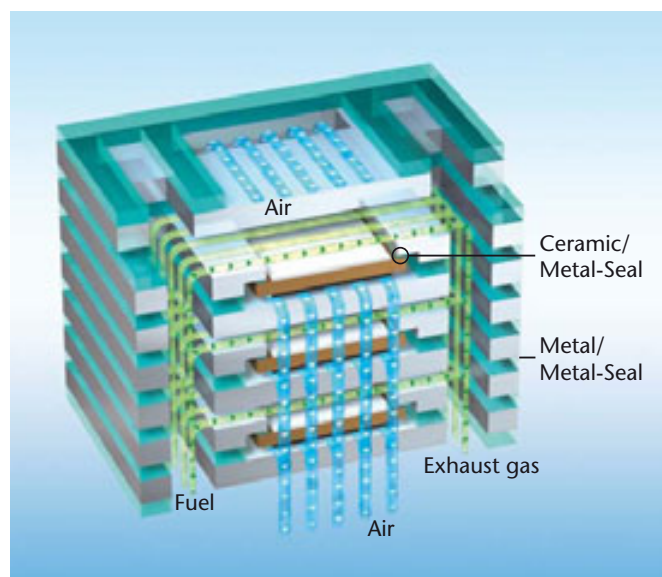


Fig. 41. Glass and Glass Ceramic Sealants

Table 10. SOFC Sealing Glasses

Glass No. Type	$\alpha_{(20/300)}$ [10 ⁻⁶ 1/K]	$\alpha_{(20/750)}$ [10 ⁻⁶ 1/K]	T_g [°C]	ρ [g/cm ³]	T_x [°C]	temp- erature at 10 ⁴ dPas	hot stage microscopy data			
							sintering temp	softening temp	hemisphere temp	flowing temp
G018-281 glass	4.6	–	652	2.7	–	1196	737	927	1270	1333
GM31107 glass	10.0	–	532	3.7	620	750	557	649	750	844
G018-315 glass ceramic	9.8 (p.c.)	11.8 (p.c.)	567	3.7	725	–	619	739	823	872
G018-311 glass ceramic	9.8 (p.c.)	12.4 (p.c.)	614	3.8	808	873	669	770	853	904
G018-304 glass ceramic composite	9.5 (p.c.)	12.7 (p.c.)	620	3.4	760	–	658	858	917	942
G018-305 glass ceramic composite	10.3 (p.c.)	13.2 (p.c.)	595	3.5	769	–	660	908	944	991

p.c. = partially crystalline

T_x = Crystallization temperature

8. Solder Glasses

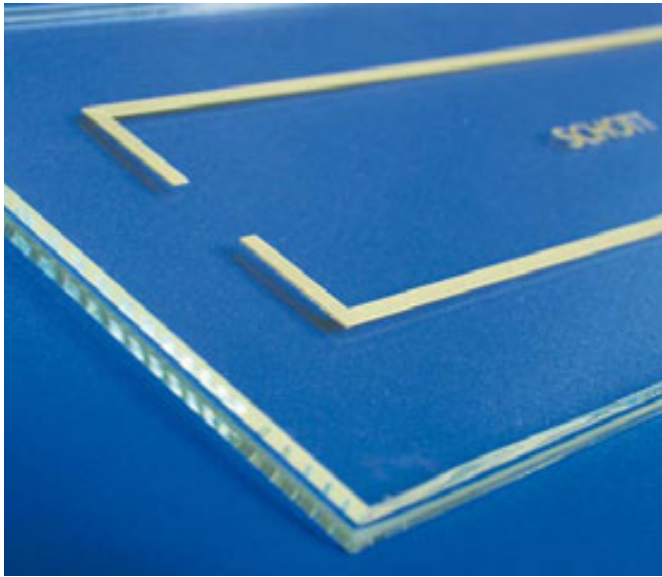


Fig. 42. Panes of flat glass AF 45 bonded with composite solder glass

Solder glasses are special glasses with a particularly low softening point. They are used to join glass to other glasses, ceramics, or metals without thermally damaging the materials to be joined. Soldering is carried out in the viscosity range $\eta = 10^4 - 10^6$ dPa·s of the solder glass (Figure 43); this corresponds to a temperature range $T_{\text{solder}} = 350 - 700$ °C.

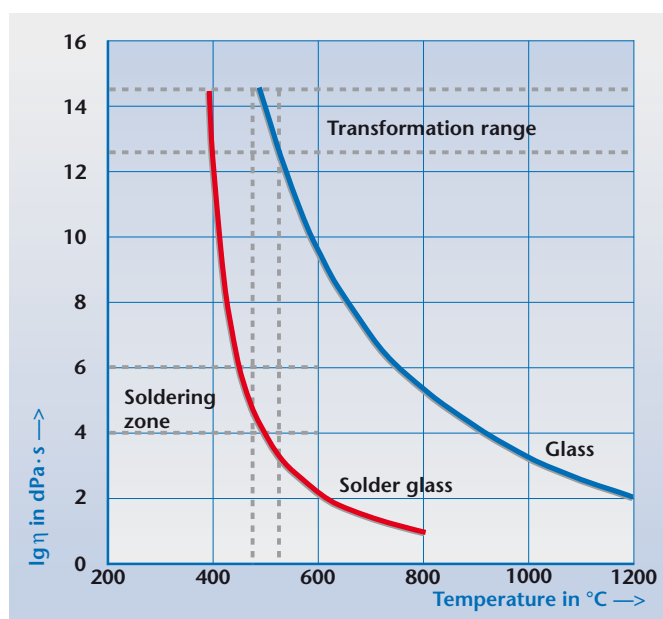


Fig. 43. Viscosities η of solder glass to be soldered

We distinguish between vitreous solder glasses and devitrifying solder glasses, according to their behavior during the soldering process.

Vitreous solder glasses behave like traditional glasses. Their properties do not change during soldering; upon reheating the solder joint, the temperature dependence of the softening is the same as in the preceding soldering process.

Unlike vitreous solder glasses, *devitrifying solder glasses* have an increased tendency to crystallize. They change into a ceramic-like polycrystalline state during soldering. The viscosity increases by several orders of magnitude during crystallization so that further flowing is suppressed. This time-dependent viscosity behavior is exemplarily shown in Figure 44 for a devitrifying solder glass processed by a specific temperature-time program.

On the other hand, crystallization allows a stronger thermal reload of the solder joint, normally up to the temperature range of the soldering process itself. Devitrifying glasses are available upon request.

The development of solder glasses with very low soldering temperatures is limited by the fact that reducing the temperature generally means increasing the coefficient of thermal expansion. This effect is less pronounced in devitrifying solder glasses. It can be even more effectively avoided by adding inert (non-reacting) fillers with low or negative coefficients of thermal expansion (e.g. ZrSiO_4 or β -eucryptite). Such *composite solder glasses* are preferably used to produce stable glass solders.

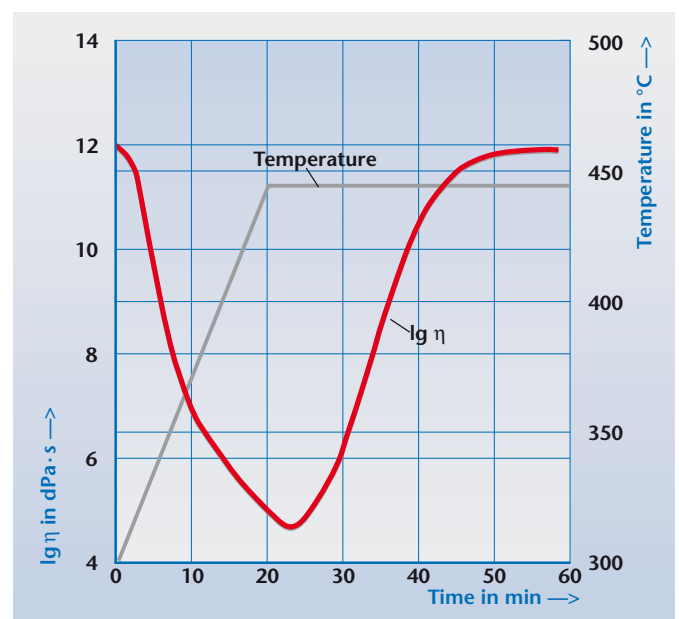


Fig. 44. Viscosity development of a crystallizing solder glass during soldering

Because fillers reduce the flow capability during the soldering process, they can be added to the batch only in limited amounts.

Taking into consideration the properties of the materials to be joined, suitable solder glasses are mainly selected under the following aspects:

1. highest permissible soldering temperature,
2. thermal expansion of the materials to be joined,
3. maximum application temperature of the solder zone,
4. chemical behavior.

Processing

To achieve satisfactory soldering, the solder glass must flow sufficiently and wet the parts to be joined well. Flow and wetting are temperature- and time-controlled; the higher the temperature, the less time is required for sufficient flow, and vice versa.

Thus, soldering at high temperatures may take only a few minutes, whereas at low temperatures (i.e., at viscosities $\geq 10^7$ dPa·s) reaching sufficient flow takes very long and usually can be achieved only under additional mechanical load.

Properties

As with all sealings involving glass, adapting the thermal expansions of the components to be joined with solder glass is a necessary prerequisite for stable, tight joints. As a rule, the coefficient of thermal expansion of the solder glasses should be by $\Delta\alpha = 0.5 - 1.0 \times 10^{-6}/\text{K}$ smaller than the expansion coefficients of the sealing partners.

The relationship between soldering temperature and thermal expansion is schematically shown in Figure 45.

With devitrifying solder glasses, one must consider that the expansion coefficients given in the respective lists of properties are only valid on condition that the specific soldering program defined for each solder glass is complied with. Changing the soldering program, in particular the soldering temperature and the soldering time, may affect the relationship between glassy and crystalline phase and thus change the coefficient of thermal expansion, with the possible result of a mismatch.

Sealing joints produced with vitreous solder glasses can be loaded to approximately 50 K below the transformation temperature of the respective solder glass. The maximum service temperature of devitrifying solder glasses depends on the type and melting point of the precipitated crystals and on the amount and properties of the residual glass phase. Up to maximum service temperature, solder glasses are moisture- and gas-proof. Their good electric insulating property is superior to that of many standard technical glasses. They are therefore also suitable as temperature-resistant insulators. The chemical resistance of solder glasses is generally lower than that of standard

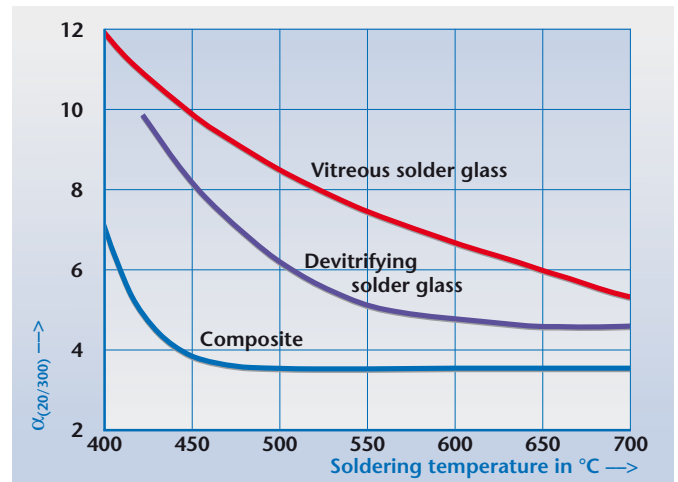


Fig. 45. Relationship between soldering temperature and linear expansion α for solder glasses. The curves describe the lowest limits for the respective solder glass types

technical glasses. Therefore, solder glass sealings can be exposed to chemically aggressive environments (e.g. acids, alkaline solutions) only for a limited time.

Deliverable forms and shapes

Solder glass can be supplied in the form of powder, granulate and sintered performs (e.g. rings, rods, ...), and as paste. An example of a glass-to-metal seal application is shown in Figure 46. Table 11 gives a selection of available SCHOTT solder glasses, Table 12 lists the grain size for all glasses supplied by SCHOTT.

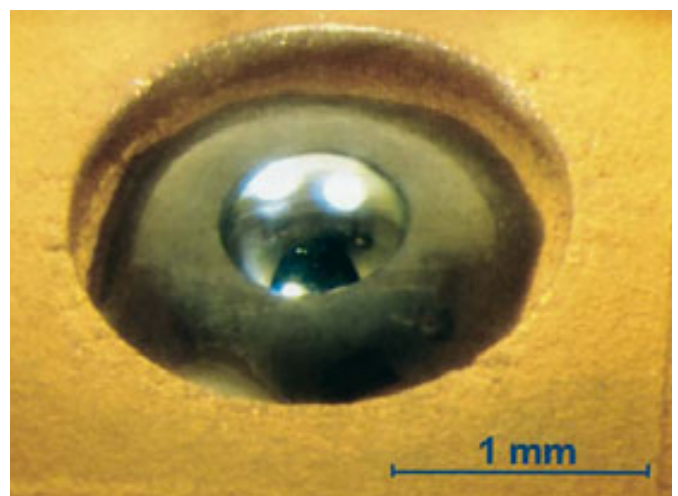
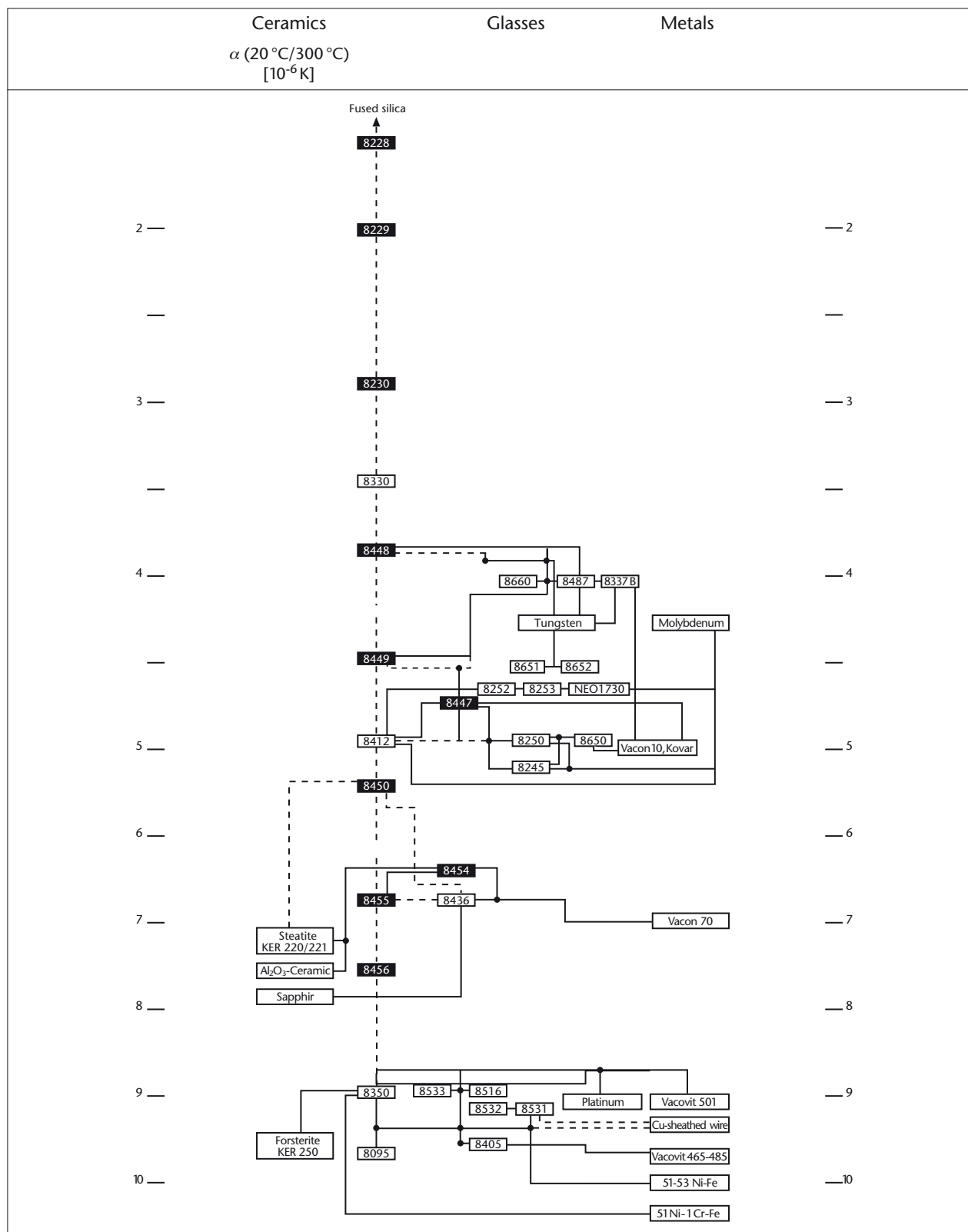


Fig. 46. Spherical lens, sealed to a metal casing with a sintered solder glass ring

Table 11. Graded seals



Technical glasses

Intermediate sealing glasses

— Tried-out, unrestricted seals with stresses ≤ 8 N/mm² at room temperature.

--- Producible seals, limited with regard to size and geometry, with stresses between 8 N/mm² and 20 N/mm² at room temperature.

Table 12. SCHOTT solder glasses

Glass No.	$\alpha_{(20/300)}$	T_g	Sealing temperature		Density	t_{k100}	$\tan\delta$
	[10 ⁻⁶ x K ⁻¹]	[°C]	[°C]	t_{holding} [min]		[g/cm ³]	[°C]
Lead containing							
G018-223	3.0	325	430	15	6.0	–	–
G017-002	3.6	540	700	15	3.6	–	37
G018-224	4.35	324	430	15	6.1	–	–
G017-339	4.7	325	450	15	4.3	11.5	19
G018-225	4.7	328	430	15	5.6	–	–
G017-712	5.3	375	510	10	–	–	–
G018-226	6.0	327	440	15	5.5	–	–
G017-393	6.5	320	425	15	4.8	11.6	15
G017-340	7.0	315	420	15	4.8	13.4	14
G018-227	7.2	317	440	15	–	–	–
G018-228	7.6	311	400	15	5.0	–	–
8465	8.2	385	460	60	5.4	14.9	27
G018-229	8.7	310	410	15	5.4	–	–
G018-256	9.6	316	420	15	5.8	–	–
G017-052	11.7	308	410	15	6.7	–	–
Lead free							
G018-250	7.0	380	540	15	5.7	–	–
G018-255	9.4	396	520	15	6.7	–	–
8470	10.0	440	680	60	2.8	–	–
G018-249	10.1	365	500	15	7.1	–	–

Other matched CTE available upon customer request

All solder glasses are available as K3 powder. Grain size: $d_{50} = 10 \pm \alpha_{\mu m}$, $d_{99} \leq 63_{\mu m}$

9. Passivation Glasses

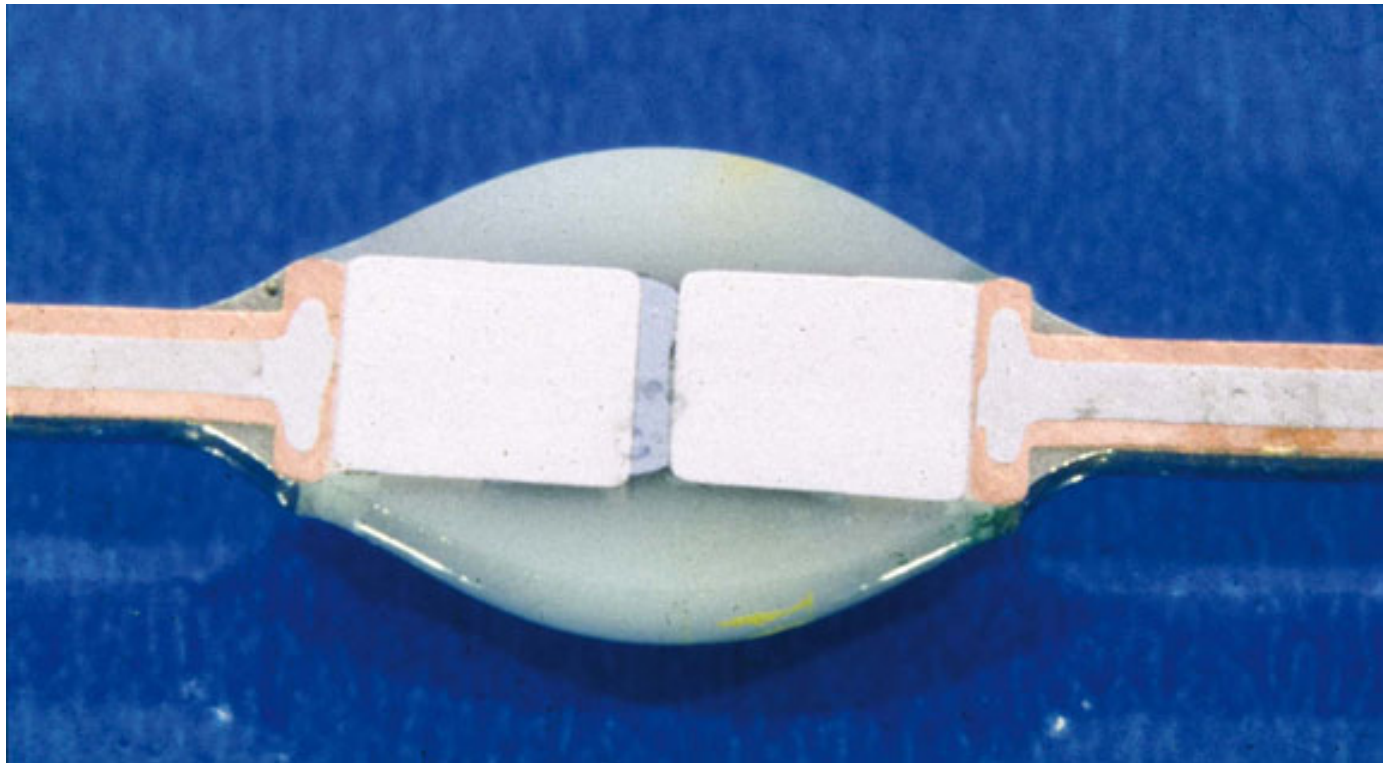


Fig. 47. Polished section of a glass-encapsulated silicon diode

Passivation glasses are zinc-borosilicate and lead-alumina silicate glasses used for chemical and mechanical protection of semiconductor surfaces.

Processing

To avoid distortion and crack formation, the different co-efficients of thermal expansion of the passivation glass and the other semiconductor components must be taken into account. If the mismatch is too large, a network of cracks will originate in the glass layer during cooling or subsequent processing and destroy the hermetic protection of the semiconductor surfaces. Basically, there are three ways of overcoming this problem:

The thinner the passivation glass layer, the smaller is the risk of cracking. SCHOTT therefore recommends maximum thicknesses for all homogeneous passivation layers that, as a rule, should not be exceeded.

The sealing stress between glass and silicon, and thus the risk of cracking, can be reduced by slow cooling in the transformation range. As a rough rule, a cooling rate of 5 K/min is suitable for passivation layers in the temperature range $T_g \pm 50$ K.

Another way of avoiding thermal expansion mismatches is using composite glasses. Composites consist of a mixture of passivation glass powder and an inert filler such as, for example, powdered ceramics with very low or negative thermal expansion. Such fillers lower the mean thermal expansion coefficient of the passivation glass and thus

minimize or eliminate the risk of cracking. As a secondary effect, fillers improve the mechanical stability of the composite glass.

Different processing techniques, adjusted to the requirements of the respective applications, are employed. For the manufacturing of sintered glass diodes usually a slurry of glass powder and deionized water is applied to the diode body, including the Mo- or W-contact studs. For wafer passivation (glass applied to the Si wafer before separating the chips) an organic suspension is applied by spinning, doctor blading, sedimentation, electrophoresis, or screen printing. The organic suspension vehicles must be completely volatile or thermally decomposable below the softening temperature of the glass.

Properties

Electrical insulation, including dielectric breakdown resistance, generally depends on the alkali content, particularly on the Na^+ content. Alkali contamination in SCHOTT passivation glasses is kept low by selecting pure raw materials and special manufacturing procedures. Contamination is tested for every batch. Typical contents are below 100 ppm for Na_2O and K_2O , and below 20 ppm for Li_2O . Some composite passivation glasses may contain fillers with slightly higher amounts of alkali; because the mobility of alkali ions is negligible, there is no risk of impairing the quality of the component.

Table 13. SCHOTT passivation glasses

Lead containing	Typ	Main applications	$\alpha_{(20/300)}$ 10 ⁻⁶ /K	T_g °C	Pb-contents wt%	Firing temp. °C	Holding Time Min.	T_j °C	Layer thickness μm
G018-205	Pb-Zn-B	sinter glass diodes	4.45	632	1–5	690	10	–	–
G017-388	Zn-B-Si composite	thyristors, high-blocking rectifiers	3.6	550	1–5	700	5	180	≥ 30
G017-002	Zn-B-Si composite	sintered glass diodes	3.7	545	1–5	700	10	180	–
G017-096R	Pb-B-Si	sinter glass, planar- and mesa-diodes	4.8	456	10–50	680	5	160	–
G017-004	Pb-B-Si composite	mesa diodes	4.1	440	10–50	740	5	160	≥ 30
G017-230	Pb-B-Si composite	transistors	4.2	440	10–50	700	4	160	≥ 25
G017-725	Pb-B-Si	sinter glass diodes	4.9	468	10–50	670	10	180	–
G017-997	Pb-B-Si composite	wafer passivation	4.4	485	10–50	760	20	180	–
G017-209	Pb-Zn-B	ICs, transistors	6.6	416	10–50	510	10	180	≤ 5
G017-980	Pb-Zn-B	varistors	6.5	393	10–50	520	30	–	–
G018-133	Pb-B-Si composite	sinter glass diodes	4.8	463	10–50	690	30	–	–
Lead-free									
G018-200	Zn-B-Si	sinter glass diodes	4.6	557	–	665	10	–	–
G018-197	Zn-B-Si	sinter glass diodes	4.4	557	–	675	10	–	–
G018-255	Bi-Zn-B	varistors	9.4	396	–	520	15	–	–

Heavy metals which are incompatible with semiconductors are controlled as well. The CuO content, for example, is below 10 ppm.

Because the mobility of charge carriers increases drastically with increasing temperature, a temperature

limit, called junction temperature T_j , is defined up to which glass-passivated components can be used in blocking operations.

In manufacturing, glass passivation is often followed by chemical processes (such as etching of contact windows or electrolytic deposition of contacts) which may attack the glass. The chemical resistance of the various passivation glasses differs strongly and is an important criteria in selecting the appropriate glass type. Zinc-borosilicate glasses, for instance, are highly sensitive to chemical attack by acids and alkaline solutions and therefore only recommended for use with contacts applied by sputtering.

Forms of supply

Passivation glasses are supplied as glass powders, ground iron-free and with negligible abrasion. For certain applications passivation glasses are available as tubing or sleeves. They are available in various grain sizes (generally type K, see Table 12) to suit the respective application.

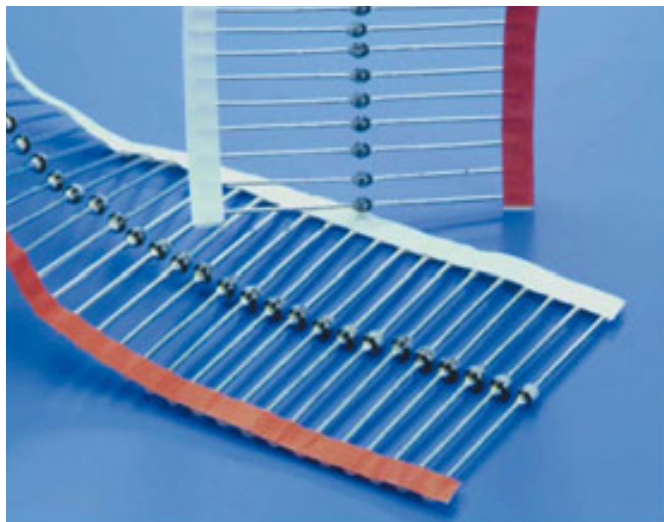


Fig. 48. Diodes prepared for delivery (e.g. small signal diodes)

10. Glass Ceramics

Glass ceramics are distinguished from glass and ceramics by their characteristic manufacturing process (see Figure 51) and by their properties. Not classifiable as glass or as ceramic, they represent a completely new material.

They are manufactured in two principal production steps. In the first step, a batch of exactly defined composition is melted (as for normal glass). The composition is determined by the desired properties of the end-product as well as by the necessary working properties of the glass. After melting, shapes are produced by pressing, blowing, rolling or casting and then annealed. In this state the material still exhibits all the typical characteristics of glass.

In the second step, the “glassy” articles are subjected to a specific temperature-time treatment between 800–1200 °C (defined for each composition), by which they are ceramized, i.e., they are transformed into a mainly polycrystalline material. Apart from the crystalline phase with crystals of 0.05–5 µm in size, this material contains a residual glass phase of 5–50%.

In the temperature range between 600–700 °C, small amounts of nucleating agents (e.g. TiO_2 , ZrO_2 or F) induce precipitation of crystal nuclei. As the temperature increases, crystals grow on these nuclei. Their type and properties as well as their number and size are predetermined by the glass composition and the annealing program. By appropriate program selection, either transparent, slightly opaque, or highly opaque, non-transparent glass ceramics can be produced. Unlike conventional ceramics, these glass ceramics are absolutely dense and pore-free. To achieve controlled crystallization in the glass, the temperature difference between the nuclei formation region and the crystal growth region must be sufficiently large (Figure 53). In this way, spontaneous crystallization during hot forming and unwanted crystal growth during nucleation can be avoided.



Fig. 49. An application of glass ceramics are Ceran® cooktop panels, e.g., the “Ceran® for Gas” family of products: a combination of electric and gas cooking zones



Fig. 50. 8.2-m telescope mirror blank, Zerodur® glass ceramic

Like the glass composition, the composition of glass ceramics is highly variable. Well-known compositions lie within the following systems:

$\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$; $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$; $\text{CaO}-\text{P}_2\text{O}_5-\text{Al}_2\text{O}_3-\text{SiO}_2$.

Glass ceramics of the $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system, that contain small amounts of alkali and alkaline-earth oxides as well as TiO_2 and ZrO_2 as nucleating agents, have achieved greatest commercial significance. Based on this system, glass ceramics with coefficients of linear thermal expansion of close to zero can be produced (Figure 52 and Table 12). This exceptional property results from the combination of crystalline constituents (such as solid solutions of *h*-quartz, *h*-eucryptite or *h*-spodumene), with negative coefficients of thermal expansion, and the residual glass phase of the system, with a positive coefficient of thermal expansion.

Such “ α -0-glass ceramics” can be subjected to virtually any thermal shock or temperature variation below 700 °C. Whereby wall thickness, wall thickness differences, and complicated shapes are of no significance.

Another technical advantage is the exceptionally high dimensional and shape stability of objects made from these materials, even when subjected to considerable temperature variations.

Zerodur® glass ceramic, whose coefficient of linear thermal expansion at room temperature can be kept at $\leq 0.05 \times 10^{-6}/\text{K}$ (Table 14), was especially developed for the production of large mirror blanks for astronomic reflecting telescopes. Further applications of Zerodur® are opto-mechanical precision pieces such as length standards, mirror spacers in lasers, and so on. With a length

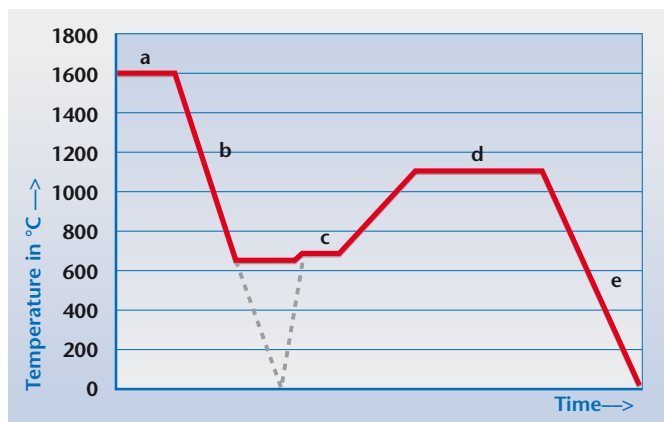


Fig. 51. Temperature-time schedule for glass ceramic production
a: melting, b: working, c: nucleation, d: crystallization, e: cooling to room temperature

ageing coefficient A ($L = L_0 (1 + A \Delta t)$, Δt = time span) below 1×10^{-7} /year, Zerodur® has excellent longitudinal stability.

PYRAN® Platinum is the world's first fire-rated glass-ceramic manufactured using the microfloat process. It offers an excellent surface quality and unprecedented color neutrality. PYRAN® Platinum is the only environmentally-friendly fire-rated glass-ceramic produced without hazardous heavy metals arsenic, antimony and barium. It is UL (Underwriters Laboratories) classified for fire-ratings up to 90 minutes and passes the required hose stream test. PYRAN® Platinum fire-rated glass-ceramic is intended for use in non-impact, safety-rated locations such as transoms and windows. The filmed and laminated PYRAN® Platinum glass-ceramic products are impact safety-rated and meet

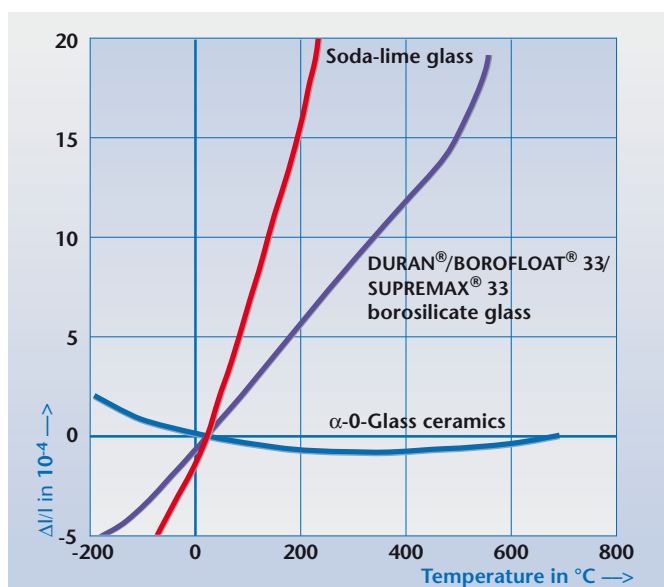


Fig. 52. Thermal expansion of α -0-glass ceramics compared to borosilicate glass 3.3 and soda-lime glass

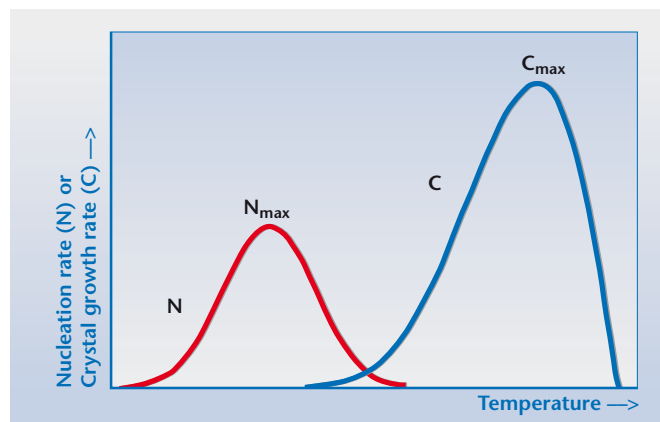


Fig. 53. Nucleation rate (N) and crystal growth rate (C) of glasses, related to temperature

the requirements according to ANSI (Cat. I and II). They are intended for use in safety-rated locations such as door lites, transoms or sidelites, and windows.

Table 14. Coefficient of linear thermal expansion α , density and elastic properties of Zerodur® and glass ceramics for cooktop panels

	Unit	Product class	Zerodur®	Glass Ceramics for cooktop panels
$\alpha_{0/50}$	$10^{-6}/K$	1	0 ± 0.05	
		2	0 ± 0.1	
		3	0 ± 0.15	
$\alpha_{20/300}$	$10^{-6}/K$		+0.1	-0.2
$\alpha_{20/500}$	$10^{-6}/K$		-	-0.01
$\alpha_{20/600}$	$10^{-6}/K$		+0.2	-
$\alpha_{20/700}$	$10^{-6}/K$		-	+0.15
Density	g/cm^3		2.53	2.56
Young's modulus E	N/mm^2		91×10^3	92×10^3
Poisson's ratio μ			0.24	0.24



Fig. 54. PYRAN® fire-rated glass-ceramic product lines pass the fire and hose stream tests.

Glass Types

The information contained in this brochure was updated in 2007.

Table 15.

8095	Lead glass (28% PbO), electrically highly insulating, for general electro-technical applications
8100	Lead glass (33.5 % PbO), electrically highly insulating highly X-ray-absorbing
8242	Borosilicate glass for Fe-Ni-Co-alloys and molybdenum, electrically highly insulating
8245	Sealing glass for Fe-Ni-Co alloys and molybdenum, minimum X-ray absorption, chemically highly resistant
8250	Sealing glass for Fe-Ni-Co alloys and molybdenum, electrically highly insulating
8252	Alkaline earth aluminosilicate glass for high temperature applications, for sealing to molybdenum
8253	Alkaline earth aluminosilicate glass for higher temperature applications, for sealing to molybdenum
NEO 1730	Alkaline earth, Neodymium containing, violet colour aluminosilicate glass for high temperature applications in electrical engineering, for sealing to molybdenum, free from alkali
8271	Borosilicate glass, highly UV-blocked, stabilised against solarisation, sealing glass for Fe-Ni-Co-alloys
8271N	Borosilicate glass, highly UV-blocked, stabilised against solarisation, sealing glass to KOVAR metal
8326	SBW glass, neutral glass tubing, chemically highly resistant
8330	DURAN®/BOROFLOAT® 33 and SUPREMAX® 33 borosilicate glass, all-purpose glass mainly for technical applications such as apparatus for the chemical industry, for pipelines and laboratory
8337B	Borosilicate glass, highly UV-transmitting, for sealing to glasses and metals of the Kovar / Vacon-10/11 range and Tungsten
8341	BOROFLOAT® 40, borosilicate floatglass adapted for prestressing
8347	Colourless, highly transmitting 8330
8350	AR-Glas®, soda-lime silicate glass
8360	Soft glass, lead-free
8405	Highly UV-transmitting soft glass
8412	FIOLAX® clear, neutral glass, chemically highly resistant, for pharmaceutical packaging
8414	FIOLAX® amber, neutral glass, chemically highly resistant, for pharmaceutical packaging
8415	ILLAX®, amber glass for pharmaceutical packaging
8436	Glass, particularly resistant to sodium vapours and alkaline solutions, suitable for sealing to sapphire
8470	Lead-free borosilicate solder glass for sealing of materials with a CTE of 10,5–11,5 x 10 ⁻⁶ K ⁻¹
8487	Sealing glass for Tungsten
8488	SUPRAX®, borosilicate glass, chemically and thermally resistant
8516	IR-absorbing sealing glass for Fe-Ni, lead-free, low-evaporating
8531	Soft glass, sodium-free, high lead content, for encapsulation of semiconductor components at low temperature (diodes)
8532	Soft glass, sodium-free, highly lead-containing, for encapsulation of semiconductor components at low temperature (diodes)
8625	IR-absorbing biocompatible glass for (implantable) transponder
8650	Alkali-free sealing glass for molybdenum, especially for implosion diodes, highly lead-containing, passivation glass
8651	Tungsten sealing glass for power and PIN diodes, passivation glass
8652	Tungsten sealing glass for power and PIN diodes, low melting passivation glass
8660	Borosilicate glass for sealing to Tungsten, of high cesium content
8708	PYRAN® Platinum, transparent floated glass-ceramic
8800	Neutral glass, highly chemical-resistant
G017-340	Low temperature sealing glass for Fe-Ni alloys
G018-197	Lead-free passivation glass for diodes and rectifiers
G018-200	Lead-free passivation glass
G018-205	Passivation glass for diodes and rectifiers
G018-249	Low melting lead-free solder glass
G018-255	Lead-free solder glass
GM39169	Lead free passivation glass

Glasses for the Chemical Industry and Electrical

Table 15. Characteristic values of technical glasses

1	2	3	4			5	6	7	8
Glass No.	$\alpha_{(20/300)}$	Transformation temperature T_g	Glass temperature at viscosities			Density at 25°C	Young's modulus	Poisson's-ratio	Heat conductivity λ at 90 °C)
			$10^{13} \text{ dPa} \cdot \text{s}$	$10^{7.6} \text{ dPa} \cdot \text{s}$	$10^4 \text{ dPa} \cdot \text{s}$				
	[10 ⁻⁶ /K]	[°C]	[°C]	[°C]	[°C]	[g/cm ³]	[10 ³ N/mm ²]	μ	[W/(m · K)]
8095	9.1	430	435	630	982	3.01	60	0.22	0.9
8100	9.6	465	465	655	960	3.28	–	–	–
8242	4.8	470	480	720	1120	2.27	57,2	0,21	–
8245	5.1	505	515	720	1040	2.31	68	0.22	1.2
8250	5.0	490	500	720	1055	2.28	64	0.21	1.2
8252	4.6	720	725	935	1240	2.63	81	0.24	1.1
8253	4.7	790	795	1005	1305	2.7	83	0.23	1.1
NEO 1730	4.5	725	725	935	1210	2.67	–	–	–
8271	4.8	480	500	725	1050	2.29	59	0.21	1.1
8271N	4.95	490	495	715	1040	2.29	60	0.21	1.1
8326	6.6	565	570	770	1125	2.45	75	0.20	1.2
8330	3.3	525	560	825	1260	2.23	63	0.20	1.2
8337B	4.1	440	465	705	1085	2.22	51	0.22	1.0
8341	4.04	577	600	840	1277	2.28	68	0.20	1.2
8347	3.3	525	560	825	1260	2.23	63	0.20	1.2
8350	9.1	525	530	720	1040	2.50	73	0.22	1.1
8360	9.1	465	470	575	745	2.66	85	0.238	–
8405	9.7	460	470	665	1000	2.51	65	0.21	1.0
8412	4.9	565	565	785	1165	2.34	73	0.20	1.2
8414	5.4	560	560	770	1155	2.42	71	0.19	1.2
8415	7.8	535	540	720	1050	2.50	74	0.21	1.1
8436	6.49	624	–	–	1085	2.785	–	–	–
8470	10.0	440	–	570	748	2.80	–	–	–
8487	3.9	525	560	775	1135	2.25	66	0.20	1.2
8488	4.3	545	560	800	1250	2.30	67	0.20	1.2
8516	8.9	447	445	646	990	2.56	72	0.21	1.1
8531	9.1	435	430	585	820	4.31	52	0.24	0.7
8532	8.7	435	430	560	760	4.46	56	0.24	0.7
8625	9.15	514	520	703	1023	2.52	73	0.22	1.1
8650	5.1	475	475	625	885	3.57	62	0.23	0.5
8651	4.4	549	540	736	1034	2.91	59	0.24	0.9
8652	4.5	495	490	638	900	3.18	58	0.25	0.9
8660	4.0	555	549	830	1215	2.44	–	–	–
8708	–0.36	–	885	–	–	2.5018	92	0.254	1.65
8800R	5.5	565	570	790	1175	2.34	73	–	–
G017-340	7.0	315	–	360	–	4.8	60	0.28	–
G018-197	4.4	557	–	–	–	3.8	–	–	–
G018-200	4.6	557	–	–	–	3.6	–	–	–
G018-205	4.5	541	–	632	–	3.8	–	–	–
G018-249	10.1	365	–	–	–	7.1	68	0.31	–
G018-255	9.4	–	–	456	528	6.7	67	0.24	–

Engineering · Sealing Glasses

9	10		11		12	13	14			15
t _{k100}	Logarithm of the electric volume resistance in Ω cm at		Dielectric properties for 1 MHz at 25 °C		Refractive index <i>nd</i> (λ _d = 587.6 nm)	Stress-optical coefficient <i>K</i> [10 ⁻⁶ mm ² /N]	Classes of chemical stability			Glass No.
[°C]	250 °C	350 °C	ε _r	tan δ [10 ⁻⁴]			Water	Acid	Alkaline solution	
330	9.6	7.6	6.6	11	1.556	3.1	3	2	3	8095
–	–	–	–	–	1.595	–	3	–	–	8100
–	–	–	–	–	1.480	–	2	–	–	8242
215	7.4	5.9	5.7	80	1.488	3.8	3	4	3	8245
375	10	8.3	4.9	22	1.487	3.6	3	4	3	8250
660	14.3	12	6.1	11	1.538	2.8	1	3	2	8252
630	13	11	6.6	15	1.547	2.7	1	2	2	8253
–	–	–	–	–	1.548	–	1	3	2	NEO 1730
390	10.3	8.6	5.4	35	1.505	4.1	3	4	3	8271
365	10.0	8.2	5.3	60	1.502	4.0	3	4	3	8271N
210	7.3	6.0	6.4	65	1.506	2.8	1	1	2	8326
250	8.0	6.5	4.6	37	1.473	4.0	1	1	2	8330
315	9.2	7.5	4.7	22	1.476	4.1	3	4	3	8337B
–	–	–	–	–	1.479	–	1	1	2	8341
250	8.0	6.5	4.6	37	1.473	4.0	1	1	2	8347
200	7.2	5.7	7.2	70	1.514	2.7	3	1	2	8350
275	8.5	6.7	7.3	24	1.566	2.9	3	4	3	8360
280	8.5	6.9	6.5	45	1.505	2.8	5	3	2	8405
215	7.4	6.0	5.7	80	1.492	3.4	1	1	2	8412
200	7.1	5.6	6.3	107	1.523	2.2	1	2	2	8414
180	6.7	5.3	7.1	113	1.521	3.2	2	2	2	8415
–	–	–	–	–	–	–	1	2-3	1	8436
295	–	–	–	–	–	3.7	1	1	2	8470
300	8.3	6.9	4.9	36	1.479	3.6	4	3	3	8487
200	7.1	5.8	5.4	96	1.484	3.2	1	1	2	8488
250	8.1	6.4	6.5	25	1.516	3.0	3	1	2	8516
450	11	9.8	9.5	9	1.700	2.2	1	4	3	8531
440	11	9.4	10.2	9	1.724	1.7	1	4	3	8532
210	7.2	5.8	7.1	68	1.525	–	3	1	2	8625
128	13.5	11.6	7.6	11	1.618	2.8	1	4	3	8650
–	11.2	10.0	6.0	31	1.552	3.6	1	4	3	8651
–	–	–	6.9	35	1.589	3.4	1	4	3	8652
550	12.7	10.7	–	–	1.486	–	3	3	3	8660
175	6.6	5.2	7.6	21.8	1.53694	–	1	3	1	8708
191	7.0	5.7	5.9	143	1.490	4.6	1	1	2	8800
316	–	–	12.8	14	–	–	–	–	–	G017-340
–	–	–	–	–	–	–	–	–	–	G018-197
–	–	–	–	–	–	–	–	–	–	G018-200
–	–	–	–	–	–	–	–	–	–	G018-205
–	–	–	–	–	–	–	–	–	–	G018-249
–	–	–	–	–	–	–	–	–	–	G018-255

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