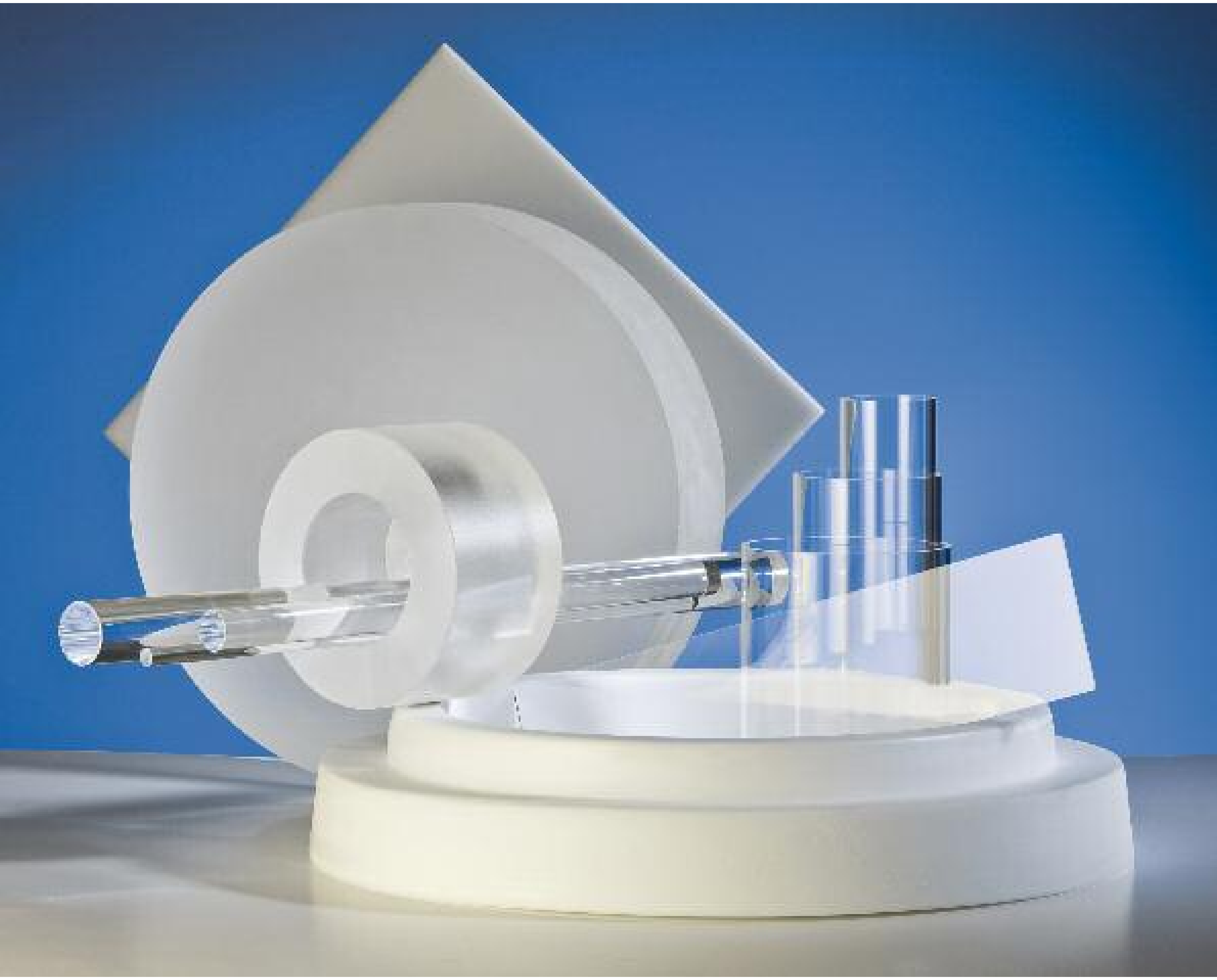
Heraeus



Base Materials
Heraeus Conamic

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The origin of today's global family-held company was the innovative vision and entrepreneurial spirit of Wilhelm Carl Heraeus, a pharmacist and chemist who took over his father's pharmacy "Einhorn-Apotheke" in Hanau, Germany in 1851.

In 1856 he succeeded in melting 2 kg of Platinum in an oxy-hydrogen flame and thus laid the basis of today's business of the Heraeus group. In 1899 Dr. Richard Küch followed in the success by fusing rock crystal into a high grade vitreous silica or "quartz glass" by the same method.

Today, Heraeus Conamic routinely manufactures fused quartz and fused silica and has been doing so for over 100 years. The know-how and excellence gained over nearly one century enables Heraeus Conamic to manufacture quartz glass solutions to the most demanding applications.

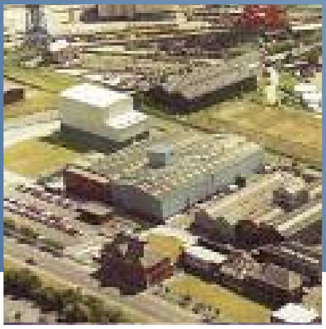
Heraeus Conamic, headquartered in Hanau, Germany, is the technology leader in manufacturing high purity quartz materials and advanced quartz components.

Heraeus Conamic supplies not only high quality fused quartz or fused silica but also specific know-how for demanding applications.

The experience of over a century has made Heraeus Conamic a global quartz glass producer with a large variety of different grades and shapes of high-purity quartz glass.

A number of unique optical, mechanical and thermal properties have made quartz glass an indispensable material in the fabrication of high-tech products.
The industrial branches working with quartz glass include semiconductor, telecommunications, lighting, solar, medical applications and chemical processing.

Heraeus Quarzglas GmbH & Co. KG, Heraeus Conamic
Kleinostheim facility, Germany



Heraeus Conamic UK Ltd.,
Wallsend facility, UK

"Einhorn" pharmacy, Hanau, Germany

Base Materials

Heraeus Conamic produces and supplies semi-finished quartz glass products. The products range from blocks and plates to cylinders and tubes. By continuous improvement of existing products and developments of in-house researchers, we provide tailored solutions to satisfy both the well known as well as the new demands and expectations of our customers.

Heraeus Conamic has mastered many different processes to supply quartz glass in almost any shape and material quality. This variety of different quartz glass grades and production routes has earned Heraeus a reputation for flexibility and innovative strength.

All processes at Heraeus Conamic comply with the most stringent certification requirements of the semiconductor industry and other high-tech companies.

On the following pages a small introduction into the nature of quartz glass is given. It shows chemical and structural properties, production routes and mechanical as well as thermal properties.

The large variety of material grades Heraeus Base Materials offers are given as examples to show the great experience we have with quartz glass.

Inspection of quartzware

Selected quartz glass products

Introduction to Quartz Glass

Artificial glass has been known for about 3500 years. Silica sand was mixed with sodium containing plant ash and chalk. The mixture was consequently heated to temperatures of 800°C to 1000°C to form glass. By mixing the melt with metal oxides glass of various colors was obtained. This glass was then used for jewelry, goblets or flasks for example. Glass made of mixtures of materials has a low melting point (around 600°C).

Quartz glass is the purest form of glass. It consists of only two elements – silicon and oxygen (SiO_2). With its high purity and its microstructure comes a unique set of properties:

- wide range of thermal stability
- low thermal expansion
- high homogeneity
- low thermal conductivity
- excellent thermal shock resistance
- high optical transmission in the IR and UV
- high chemical resistance
- low dielectric loss

Due to these properties quartz glass is one of the most valuable materials used in science and industry.

Heraeus Conamic offers not only transparent quartz glass of various material grades made through different production routes but also opaque quartz glass. Through the inclusion of bubbles the otherwise transparent quartz glass becomes opaque. The size and shape of these bubbles determine the reflection properties of the material.

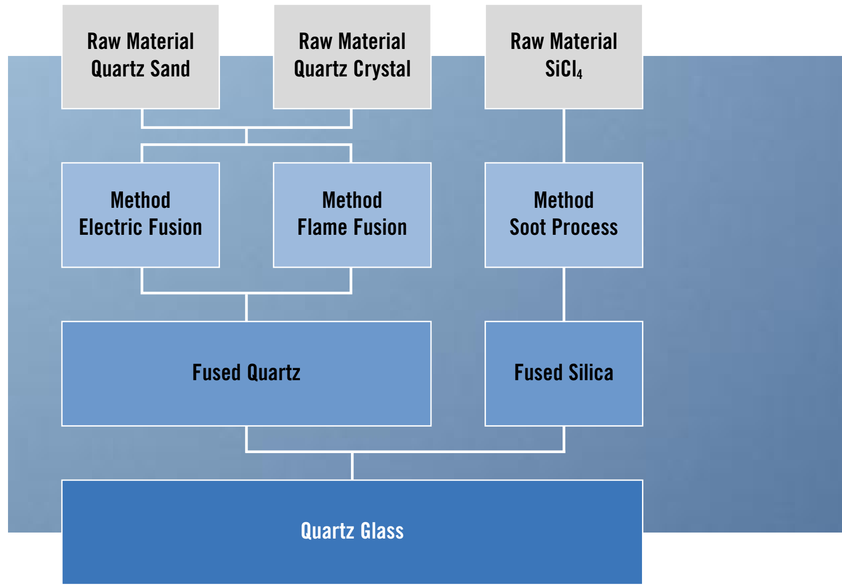
Heraeus Base Materials offers opaque grades: OM® 100, OFM® 70, OFM® 370, OFM® 970 and an opaque coating HRC.

Quartz crystal

Manufacturing of Quartz Glass

Quartz glass can be separated in two groups, distinguished by their starting material. If natural raw material (e.g. quartz sand or quartz crystal) is used, it is called fused quartz. If chemical precursors (e.g. $SiCl_4$) are used, it is called fused silica. The production method depends on the raw material. There are three established processes:

- **Electric fusion**
- **Flame fusion**
- **Soot process**



Manufacturing processes of quartz glass

Electric Fusion

The electric fusion is the most commonly used melting process for manufacturing quartz glass. Two methods of electric fusion can be used: arc melting and resistance heated furnaces.

In the arc melting an electric voltage is applied between two electrodes. If voltage and current are high enough a gas discharge forms between the electrodes. The gas discharge is also called plasma and can have temperatures of a few thousand degrees. The arc is moved above a layer of sand and melts the sand to glass. Depending on the purity and grain size distribution of the sand the resulting glass is either opaque, translucent or transparent. The arc melting is often used to form glass bodies of rotational symmetry.

Electric fusion process

The resistance heated process can be subdivided into continuous process and batch (boule) process.

In the continuous method, quartz sand is poured into the top of a vertical melter that consists of a refractory metal crucible surrounded by electric heating elements. The crucible is maintained in a neutral or slightly reducing atmosphere that prevents oxidation of the refractory metal. At temperatures exceeding 1800 °C the ordered microstructure of crystalline quartz changes to the irregular glass network. The melted material exits the bottom orifice of the crucible which is shaped to produce rods, tubes, plates or other products of various dimensions.

In the batch fusion method, a large quantity of raw material is placed inside a refractory lined vacuum furnace chamber. This method is used to produce large single boules of material.

Heraeus Base Materials offers the following electrically fused material: HSQ® 100, HSQ® 300, HSQ® 330, HSQ® 400, HSQ® 700.

Manufacturing of Quartz Glass

Flame Fusion

Heraeus chemist Richard Küch first began fusing quartz rock crystal in a hydrogen/oxygen (H_2/O_2) flame more than 100 years ago. Since then Heraeus has been producing quartz glass on an industrial scale with this process.

The basic concept of this process consists of trickling fine silica sand into a high temperature flame. In the flame the crystalline particles melt and fuse together to form quartz glass. There are different ways of removing the glass from the flame. On one hand, this can be done by fusing the trickling sand onto a bait rod and removing it to get a round ingot. On the other hand, it can be done by fusing the grains in a bowl and subsequently withdraw the glass in any desired shape through an outlet in the bottom of the bowl (ingots, cylinders and blocks).

Depending on the process parameters a transparent or an opaque quartz glass can be produced.

Heraeus Base Materials offers the following flame fused materials: HSQ® 351, HSQ® 751, TSC-3®, TSC-4

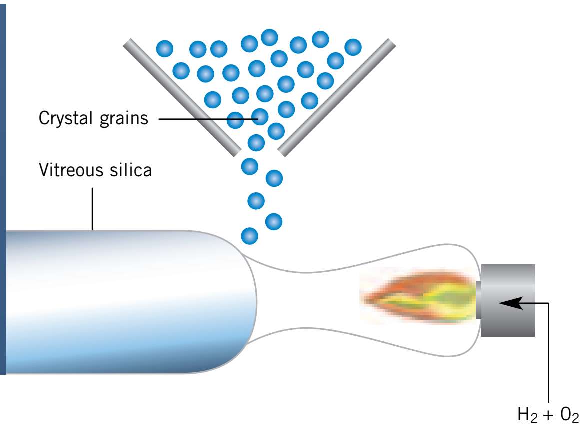
Soot Process

In this process chemical precursors (e.g. silicon tetrachloride, $SiCl_4$) are oxidized (burned) in a H_2/O_2 flame. The forming SiO_2 is deposited on a rotating bait rod like smoke off a candle deposits on a stick above the flame. The soot body is then vitrified into a transparent glass body.

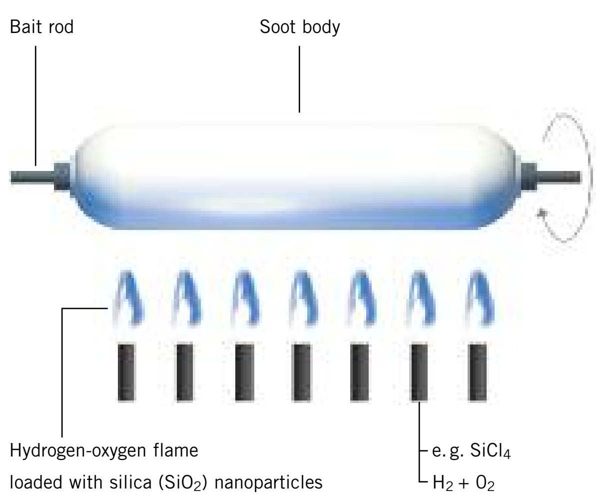
Because the precursors are made in an industrial chemical process, the raw materials have exceptionally high purity. Glass made of these precursors has an alkali- and metal ion content in the parts per billion (ppb) range.

Heraeus Base Materials offers the following synthetic materials: HSQ® 900

Flame fusion process



Soot process



Properties of Quartz Glass

Structural Background

At first glance, quartz glass appears very simple, both chemically and structurally, since it is made of a single oxide component (silicon dioxide-SiO_2).

SiO_2, containg mineral, known as Silica are found throughout the earth's crust. However, only a very small fraction has sufficient purity (>99.98%) to be suitable as raw material for quartz glass.

The generalized atomic structure consists of tetrahedral (four-faces) units constructed of four oxygen atoms surrounding a central silicon atom. These tetrahedra are connected at the corners to form a three-dimensional network. Whereas the tetrahedra in crystalline quartz form well ordered regular rings, in quartz glass the network is made of distorted and irregularly shaped loops.

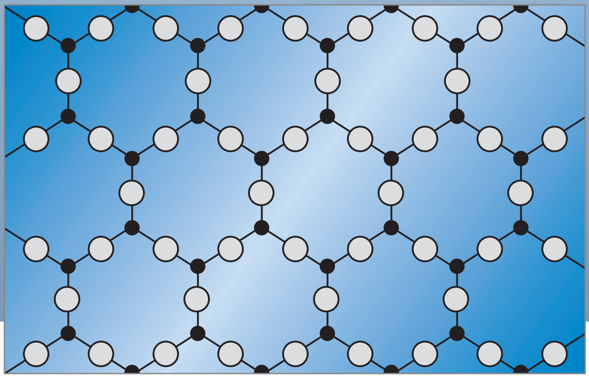
In every material increasing temperatures correspond to atoms oscillating more strongly around their position in the network, requiring more space (thermal expansion). The two networks react very differently on this oscillation. While the ordered network rearranges at specific temperatures (each structural modification has its own name), the irregular network can absorb the increasing vibrations of the atoms because the network is not as closely packed. This results in a very low thermal expansion of quartz glass.

The disordered structure is typical for any glass ("super-cooled liquid") and gives quartz glass its ability to withstand not only high temperatures but drastic temperature changes as well. Additionally it is responsible for the formability of quartz glass.

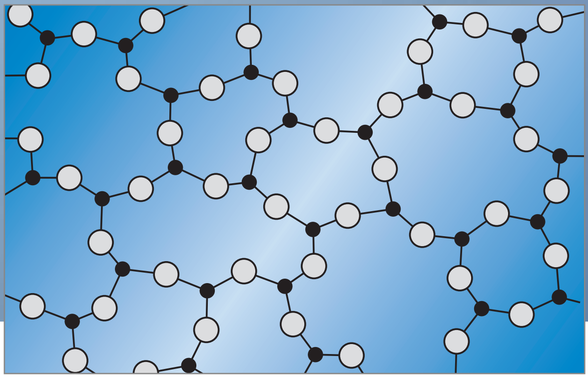
The term "super-cooled liquid" refers to the fact that, at least from the thermodynamic equilibrium point of view, quartz glass should actually be a crystalline solid rather than a liquid. This fact is the key to understanding why quartz glass devitrifies. Although the thermodynamically preferred state of quartz glass is crystalline, the high viscosity prevents the structural rearrangement necessary to achieve it. In other words, the molecules cannot arrange themselves quickly enough compared to the relatively fast rate of cooling that quartz glass experiences during production. However, under certain conditions this constraint can be removed resulting in the glass reverting to a crystalline state. This usually happens at elevated temperatures in the presence of a contaminant that drops the viscosity by breaking up the highly connected silicon-oxygen network as well as acting as a nucleating source. Alkalis like sodium or potassium are the most common contaminants that cause devitrification.

Devitrified areas can only be seen when the crystalline structure undergoes a phase transition at specific temperatures (275 °C) accompanied by volume contraction.

Crystalline SiO_2 structure



Glassy SiO_2 structure



Properties of Quartz Glass

Chemical Characteristics

Fused quartz is outstandingly resistant to most liquids (metals, solutions, acids etc.). It is corroded by hydrofluoric and phosphoric acid as well as bases. Quartz glass is sensitive to traces of alkaline and alkaline earth metals because they hasten devitrification at elevated temperatures.

Quartz glass is a very pure material consisting of SiO_2. Traces of other elements are called impurities. Despite their very low concentrations, these impurities can have a significant effect on quartz glass. A proprietary grain purification process of Heraeus guarantees an extraordinary low level of alkaline and transition metal impurities of fused quartz. Purity is predominantly determined by the raw material used. Additional possibilities for contamination arise from the manufacturing method and the handling procedures. Precautions at all stages of the production process assure a high level of purity.

The most common impurities are metals (such as Al, Na and Fe among others), water (present as OH-groups) and chlorine. These foreign elements are mainly integrated in the glass network and effect viscosity, optical absorption and electrical properties. They can also influence the properties of material processed in contact with the quartz glass during the end user application.

The purities of fused quartz and fused silica are outstandingly high. Synthetic fused silica from Heraeus contains a total metallic contamination below 1 part per million (ppm). For fused quartz the amount is approximately 20 ppm and consists primarily of Al_2O_3 with much smaller amounts of alkalis, Fe_2O_3, TiO_2, MgO and ZrO_2.

Metallic impurities come mostly from natural quartz. Very carefully controlled processes are used to greatly reduce impurities in raw materials from 200 ppm to less than 20 ppm (SiO_2-purity of 99.998%).

Aluminum, as the most prevalent element in the material, bonds directly into the quartz glass by substituting silicon atoms. Thus it has very low mobility even at high temperatures which makes it almost impossible to remove at any stage of the production process.

Small amounts of aluminum increase the viscosity of the quartz glass, allowing higher working temperatures.

Chemical Purity – Trace element concentration (ppm)

Typical Values (= Statistical Average Value)

	Li	Na	K	Mg	Ca	Fe	Cu	Cr	Ni	Mn	Ti	Zr	Al	OH
Electrically fused quartz														
HSQ® 100/300/400*	0.5	0.2	0.3	< 0.03	0.5	0.1	0.01	< 0.01	< 0.01	< 0.03	1.1	1.0	15	<30**
HSQ® 330	0.5	0.1	0.2	< 0.03	0.5	0.1	< 0.01	< 0.01	< 0.01	< 0.03	1.1	1.0	15	<30**
HSQ® 700	< 0.01	< 0.02	0.1	< 0.03	0.4	0.1	< 0.01	< 0.01	< 0.01	< 0.01	1.1	1.0	15	<30**
OM® 100	0.1	0.1	0.2	< 0.03	0.4	0.1	< 0.01	< 0.01	< 0.01	< 0.03	1.1	1.0	15	n. s.
Flame fused quartz														
TSC®-3	0.2	0.3	0.2	< 0.01	0.4	0.05	< 0.01	< 0.01	< 0.01	< 0.01	1.1	0.8	15	170
TSC-4	0.04	0.2	0.08	< 0.01	0.7	0.1	< 0.01	< 0.01	< 0.01	< 0.01	1.3	0.7	8	170
HSQ® 351	0.3	0.6	0.6	< 0.03	0.6	0.1	< 0.01	< 0.01	< 0.01	< 0.03	1.1	1.0	15	175
HSQ® 751	0.1	< 0.03	0.1	0.1	0.7	0.1	< 0.01	< 0.01	< 0.01	< 0.01	1.4	0.8	8	175
Arc fused quartz														
OFM® 70	4	20	40	9	30	50	0,4	0,4	0,2	1	110	20	210	n. s.
OFM® 370	0.5	0.7	0.6	< 0.05	0.4	0.2	< 0.05	< 0.05	< 0.05	< 0.05	1.2	1.2	15	n. s.
OFM® 970	< 0.01	0.04	0.05	0.01	0.05	0.1	0.02	0.02	< 0.01	< 0.01	0.05	0.03	11	n. s.
Synthetic fused silica* **														
HSQ® 900	< 0.002	< 0.01	< 0.01	< 0.01	< 0.02	< 0.03	<0.001	<0.001	n. s.	<0.0005	< 0.03	<0.04	<0.04	0.2

* HSQ® 400: Higher aluminium content on the outer surface due to chemical stabilization coating. *** Chlorine content: HSQ® 900: 1500ppm,

Hydroxyl Content

In addition to the metallic impurities, fused quartz and fused silica also contain water present as OH-groups. Incorporation of OH-groups into the glass network weakens its stability resulting in a lower viscosity and thus lower working temperatures. Other physical properties are also affected, such as the optical transmission by the formation of absorption bands in the infrared (IR). Each production route corresponds to a typical hydroxyl content.

- The lowest values are achieved by electrical fusion (<1-30 ppm) because the glass is melted in vacuum or in a slightly reducing atmosphere. The hydroxyl content in this range can be influenced by the moisture level during annealing processes.
- Flame fusion results in significantly higher hydroxyl levels (150-200 ppm) since fusion occurs in a hydrogen/oxygen flame.
- Synthetic fused silica produced by flame hydrolysis of chemical precursors has the highest hydroxyl content (up to 1000 ppm). This can be reduced, for instance by hot chlorination steps, to desired levels.

Physical Properties

Beyond its high purity and arising from its microstructure, quartz glass has more exceptional properties:

- As mentioned before quartz glass has a very low thermal expansion coefficient and a very high thermal shock resistance. Additionally it has a low thermal conduction.
- It has a high tensile strength that is limited in practice by the surface condition of the glass. Small defects like scratches are the point of origin for a fracture of the glass network and consequent breaking of the glass under tensile load.
- Fused quartz and fused silica are excellent insulators. Electrical conduction occurs not by electrons but by mobile ions. All foreign ions in the glass network can contribute to an electric conduction. The mobility of ions however, is strongly dependent on the charge and size of the ions and on temperature. With increasing temperature the resistivity of quartz glass decreases as the mobility of the ions increases. Because of the low concentration of impurities the conductivity of quartz glass is very small.
- Quartz glass has a very broad window of optical transmission ranging from approx. 0.180 microns to over 3.5 microns with an absorption band at 2.73 microns depending on OH content. The IR-absorption edge arises from lattice vibrations and its position depends on the thickness of the glass. The exact position of the UV absorption edge is strongly influenced by chemical elements in the glass network (impurities or dopants).

Properties of Quartz Glass

Technical Properties (Typical Values)

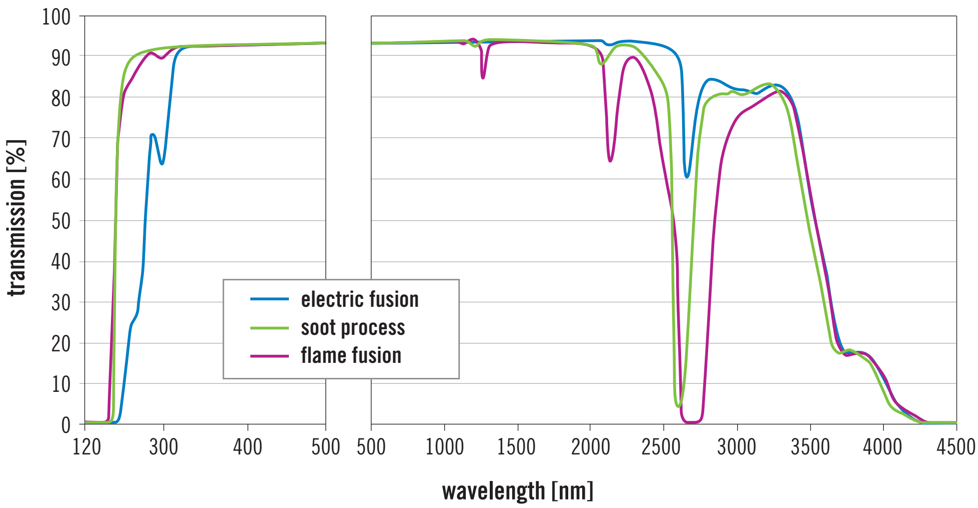
	Electric Fused Quartz	Flame Fused Quartz	Fused Silica
Mechanical Data			
Density g/cm³	2.203	2.203	2.201
Mohs Hardness	5.5 … 6.5	5.5 … 6.5	5.5 … 6.5
Micro Hardness N/mm²	8600 … 9800	8600 … 9800	8600 … 9800
Knoop Hardness N/mm²	5800 … 6100	5800 … 6100	5800 … 6200
Modulus of elasticitiy (at 20°C) N/mm²	7.25×10^4	7.25×10^4	7.0×10^4
Modulus of torsion N/mm²	3.0×10^4	3.1×10^4	3.0×10^4
Poisson's ratio	0.17	0.17	0.17
Compressive strength (approx.) N/mm²	1150	1150	1150
Tensile strength (approx.) N/mm²	50	50	50
Bending strength (approx.) N/mm²	67	67	67
Torsional strength (approx.) N/mm²	30	30	30
Sound velocity m/s	5720	5720	5720
Thermal Data			
Softening temperature °C	1710	1660	1600
Annealing temperature °C	1220	1160	1100
Strain temperature °C	1125	1070	1000
Max. working temperature continuous °C	1160	1110	950
short-term °C	1300	1250	1200
Mean specific heat J/kg·K			
0…100 °C	772	772	772
0…500 °C	964	964	964
0…900 °C	1052	1052	1052
Heat conductivity W/m·K			
20 °C	1.38	1.38	1.38
100 °C	1.47	1.47	1.47
200 °C	1.55	1.55	1.55
300 °C	1.67	1.67	1.67
400 °C	1.84	1.84	1.84
950 °C	2.68	2.68	2.68
Mean expansion coefficient K^{-1}			
0…100 °C	5.1×10^{-7}	5.1×10^{-7}	5.1×10^{-7}
0…200 °C	5.8×10^{-7}	5.8×10^{-7}	5.8×10^{-7}
0…300 °C	5.9×10^{-7}	5.9×10^{-7}	5.9×10^{-7}
0…600 °C	5.4×10^{-7}	5.4×10^{-7}	5.4×10^{-7}
0…900 °C	4.8×10^{-7}	4.8×10^{-7}	4.8×10^{-7}
-50…0 °C	2.7×10^{-7}	2.7×10^{-7}	2.7×10^{-7}

Electrically Data (Typical Values)

	Electric Fused Quartz	Flame Fused Quartz	Fused Silica
Electrical resistivity in Ω x cm			
20 °C	10^{18}	10^{18}	10^{18}
400 °C	10^{10}	10^{10}	10^{10}
800 °C	6.3×10^{6}	6.3×10^{6}	6.3×10^{6}
1200 °C	1.3×10^{5}	1.3×10^{5}	1.3×10^{5}
Dielectric strength in kV/mm (sample thickness ≥ 5 mm)			
20 °C	25 … 40	25 … 40	25 … 40
500 °C	4 … 5	4 … 5	4 … 5
Dielectric loss angle (tg δ)			
1 kHz	5.0×10^{-4}	5.0×10^{-4}	5.0×10^{-4}
1 MHz	1.0×10^{-4}	1.0×10^{-4}	1.0×10^{-4}
3×10^{10} Hz	4.0×10^{-4}	4.0×10^{-4}	4.0×10^{-4}
Dielectric constant (ε)			
20 °C 0…10^{6} Hz	3.70	3.70	3.70
23 °C 9×10^{8} Hz	3.77	3.77	3.77
23 °C 3×10^{10} Hz	3.81	3.81	3.81

Typical Transmission Spectrum (including Fresnel reflection losses)

Sample thickness: 10 mm



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The data in this brochure are valid for July 2019. We reserve the right to make alterations.

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