

UV-TRANSPARENT GLASS

The invention relates to a glass which has a good transparency to UV radiation. Said glass is also intended to have a good hydrolytic resistance and a low thermal expansion, it being intended that the thermal expansion is such that the glass produces a pressurized glazing with Al_2O_3 and, in addition, can form a seal with tungsten.

In order to ensure an optimum economic utilization of the glass, the properties of the glass should be such that it can be used, on the one hand, as window glass of EP-ROMs and, on the other hand, as a lamp for UV irradiation.

The term EP-ROM is the abbreviation for Erasable Programmable - Read Only Memory. This is a specific "read-only semiconductor store". In this semiconductor, the stored program can be erased by ultraviolet (UV) radiation. To hold the semiconductor, use is made of a housing of aluminum oxide ceramic which contains a window of highly UV-transparent glass. The UV transparency of the glass should be at least 70% for the wavelength 253.7 nm and a glass thickness of 1 mm. The glass window has to be sealed into the Al_2O_3 housing so that the interior of the housing is isolated in a gastight manner. This is achieved by using a glass with a lower thermal expansion than the Al_2O_3 ceramic. As the glass-ceramic seal cools, the ceramic housing shrinks onto the glass windows, seals the interior space in a gastight manner and places the glass under compressive stress. In order to guarantee the long-term use of the EP-ROMs even in countries with high atmospheric humidity, the glass windows must have a good hydrolytic resistance.

UV-transparent lamps are needed, for example, for therapeutic treatment or for sterilization. UV rays below 254 nm are harmful for therapeutic purposes, while UV rays up to 185 nm are important for sterilization. The production of lamps assumes that the glass used can form a seal with tungsten, Vacon 10 (Al_2O_3 and Ni/Fe/Co alloy) or molybdenum.

A UV-transparent glass is known from British Patent Specification 589,533. The glass described there contains 50 - 70% by weight of SiO_2 , 4 - 10% by weight of Al_2O_3 , 1 - 5% by weight of alkali-metal oxide and 20 - 40% by weight of B_2O_3 . The teaching therein states that the alkali-metal oxide content should be kept as low as possible to produce a UV-transparent glass.

A further UV-transparent glass is known from the Japanese Patent Application 85-21830. This has the following composition: 60 - 70% by weight of SiO_2 , 4 - 8% by weight of Al_2O_3 , 18 - 25% by weight of B_2O_3 , 6 - 11% by weight of $\text{Li}_2\text{O}+\text{Na}_2\text{O}+\text{K}_2\text{O}$, 0 - 4% by weight of $\text{MgO}+\text{CaO}+\text{SrO}+\text{BaO}+\text{ZnO}$ and 0 - 3% by weight of F_2 . The glass has a coefficient of thermal expansion α of 5.0 to $5.8 \times 10^{-6} \text{K}^{-1}$ at 30 to 380°C.

The glasses known from the literature can in each case be used for specific purposes, such as, for example, for producing UV lamps or EP-ROM windows. However, no UV-transparent glass is known which is suitable for various possible applications.

The object of the invention is therefore to provide a UV-transparent glass which is suitable for several applications. In particular, the new glass is intended to be used both for EP-ROM windows and for UV lamps.

According to the invention, this object is achieved by providing a glass which, for a wall thickness of 1 mm and a wavelength of 253.7 nm, has a transparency of at least 75%, a linear coefficient of thermal expansion of 3.8×10^{-6} to $4.5 \times 10^{-6} \text{K}^{-1}$ in the temperature range from 20 to 300°C, and a hydrolytic resistance of <120 μg of $\text{Na}_2\text{O/g}$ according to DIN 12 111. The glass according to the invention with the said properties has the following synthesis composition, calculated on an oxide basis:

SiO_2	64.0	to	66.5	per cent by weight
B_2O_3	20.0	to	22.5	per cent by weight
Al_2O_3	4.0	to	6.0	per cent by weight
Li_2O	0.4	to	1.0	per cent by weight
Na_2O	1.0	to	3.5	per cent by weight
K_2O	1.0	to	2.5	per cent by weight

CaO	0.35 to 0.8 per cent by weight
BaO	0.5 to 2.0 per cent by weight
F ⁻	0.5 to 2.0 per cent by weight
$\Sigma \text{Li}_2\text{O} * \text{Na}_2\text{O} + \text{K}_2\text{O}$	3.8 to 5.5 per cent by weight
$\Sigma \text{CaO} + \text{BaO}$	1.0 to 2.5 per cent by weight
one or more refining agents	0.2 to 2.0 per cent by weight
one or more reducing agents	0.05 to 0.3 per cent by weight

It is produced under conditions usual in glass production.

It is known that the UV transparency of the glass can be improved by reducing the iron content. Equally as important as the reduction of the total iron content is the most complete reduction possible of the iron to Fe^{2+} . The glasses must therefore not contain any oxidizing agents, such as nitrate, or refining agents, such as As_2O_3 or Sb_2O_3 .

It is also known that the glasses with a high boric acid content can be refined fairly well with NaCl. However, other refining agents are also possible. Sugar or aluminum powder is preferably used for reduction.

Investigations revealed that a UV glass can be used both for EP-ROM windows and for UV lamps if the thermal expansion - as one parameter - can be adjusted to 3.8 to $4.5 \times 10^{-6} \text{K}^{-1}$. According to the invention, this adjustment of the thermal expansion is achieved by an alkali-metal oxide content of 4.0 to 5.0% by weight and an alkaline-earth metal oxide content of 1.0 to 2.5% by weight.

Glasses with a high boric acid content are known to have very poor hydrolytic properties. Surprisingly, it was found that the high requirements imposed on the hydrolytic resistance are fulfilled if the ranges for the alkali-metal oxides and alkaline-earth metal oxides according to the invention are maintained.

An Li_2O content of 0.5% by weight to 1.0% by weight lowers the melting point. An Li_2O content of

over 1.0% by weight has an adverse effect on the hydrolytic resistance. An Na_2O content of over 3.5% by weight also affects the hydrolytic resistance adversely. Only CaO and BaO are suitable as alkaline earths. Even small quantities (for example, 0.30% by weight) of MgO result in opacification of the glass. CaO also results in a slight opacification of the glass; according to the invention, the upper limit for CaO is therefore 0.8% by weight. CaO has, on the other hand, a very favorable effect on the hydrolytic resistance; the glass should therefore contain at least 0.35% by weight of CaO . The BaO also contributes to improving the hydrolytic resistance; the total of $\text{CaO} + \text{BaO}$ should therefore be at least 1.0% by weight. Although it is possible to use SrO instead of BaO , it is not very advisable owing to the higher costs.

The Al_2O_3 content should not exceed 6.0% by weight. On the one hand, the working point V_A (V_A = working point for 10^4 dPas) rises to over 1160°C and, on the other hand, it has been found that the hydrolytic resistance becomes poorer if the Al_2O_3 content exceeds 6.0% by weight. With an Al_2O_3 content below 4% by weight, the glass becomes milky. A B_2O_3 content of over 22.5% by weight also has an adverse effect on the hydrolytic resistance. A fluorine content of 0.5 to 2.0% by weight improves the fusion and refining behavior without having an adverse effect on the UV transparency.

Table 1 below shows examples of the glass compositions according to the invention in per cent by weight. The glasses were produced by fusing the following low-iron raw materials: SiO_2 as sand (low in Fe_2O_3 ; trade name Sipur), B_2O_3 as boric acid; Al_2O_3 as $\text{Al}(\text{OH})_3$; Li_2O , K_2O , CaO and BaO as carbonate and NaCl ; F^- as Na_2SiF_6 ; NaCl was used as refining agent and sugar as reducing agent.

The glasses were fused in a quartz crucible for 1.5 to 2.5 hours at between 1500 and 1650°C (preferably, 1550°C) and refined for 2.5 to 4 hours at between 1450 and 1600°C (preferably, 1500°C).

Table 2 contains the physical and chemical properties of the glasses in Table 1.

The linear thermal expansion α was measured from 20 to 300°C. The α values are between 3.8 and $4.5 \times 10^{-6} \text{K}^{-1}$. T_g signifies the transformation point in °C. The working point V_A in °C is the temperature for a glass viscosity of 10^4dPas . The hydrolytic resistance H is determined according to DIN 12 111 in μg of Na_2O per g of glass. The UV transparency τ was determined on specimens 1 mm thick for the wavelength of 253.7 nm.

Table 1: Chemical composition in per cent by weight

	Glass 1	Glass 2	Glass 3	Glass 4	Glass 5	Glass 6	Glass 7	Glass 8	Glass 9	Glass 10	Glass 11
SiO ₂	64.65	64.65	65.65	64.65	65.15	64.15	64.85	65.65	66.30	65.50	64.60
B ₂ O ₃	22.20	21.20	22.20	22.20	22.00	22.20	22.20	21.20	20.00	21.70	21.70
Al ₂ O ₃	5.00	6.00	4.00	5.00	5.00	5.00	4.70	4.60	6.00	4.60	5.00
Li ₂ O	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.50	0.60	1.00
Na ₂ O	1.30	1.30	1.30	0.80	1.50	1.30	1.70	1.60	2.50	1.60	1.60
Na ₂ O*	(1.05)	(1.05)	(1.05)	(1.05)	(1.05)	(1.05)	(0.2)	(0.7)	(0.7)	(0.70)	(0.70)
K ₂ O	1.50	1.50	1.50	2.00	1.00	2.00	1.80	1.80	1.00	1.80	1.80
CaO	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.40	0.50
BaO	0.90	0.90	0.90	0.90	0.90	0.90	1.50	1.20	0.50	1.20	1.20
F ⁻	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60
NaCl	1.50	1.50	1.50	1.50	1.50	1.50	0.30	1.00	1.00	1.00	1.00
Sugar	0.12	0.12	0.12	0.12	0.10	0.12	0.175	0.15	0.15	0.12	0.12
Total	100.12	100.12	100.12	100.12	100.10	100.12	100.175	100.15	100.15	100.12	100.12
Σ R ₂ O	4.60	4.60	4.60	4.60	4.3	5.10	4.45	4.85	4.70	4.70	5.10
Σ R ₀	1.50	1.50	1.50	1.50	1.50	1.50	2.10	1.80	1.10	1.60	1.70

Na₂O* from NaCl

Σ R₂O also contains Na₂O as NaCl

Table 2: Physical and chemical properties

	Glass 1	Glass 2	Glass 3	Glass 4	Glass 5	Glass 6	Glass 7	Glass 8	Glass 9	Glass 10	Glass 11
α	4.06	4.04	3.91	3.99	3.89	4.11	4.01	4.03	4.17	3.96	4.07
T_g	431	444	441	444	437	442	431	440	440	436	429
V_A	1125	1153	1104	1107	1125	1103	1105	1099	1156	1123	1073
d	2.210	2.213	2.209	2.207	2.209	2.213	2.218	2.228	2.213	2.213	2.225
H	78	105	33	64	109	73	49	32	92	100	84
γ	87	87	86	81	87	86	84	86	83	85	79



claims

1. A glass transparent to UV radiation, which, for a thickness of 1 mm and the wavelength of 253.7 nm, has a transmission of at least 75%, a linear coefficient of thermal expansion of 3.8×10^{-6} to $4.5 \times 10^{-6} \text{K}^{-1}$ in the temperature range from 20 to 300°C, and a hydrolytic resistance of < 120 µg of Na₂O/g according to DIN 12 111, the glass having been produced from the synthesis composition, calculated on an oxide basis, of

SiO ₂	64	to 66.5 per cent by weight
B ₂ O ₃	20	to 22.5 per cent by weight
Al ₂ O ₃	4	to 6 per cent by weight
Li ₂ O	0.4	to 1 per cent by weight
Na ₂ O	1.0	to 3.5 per cent by weight
K ₂ O	1.0	to 2.5 per cent by weight
CaO	0.35	to 0.8 per cent by weight
BaO	0.5	to 2.0 per cent by weight
F ⁻	0.5	to 2.0 per cent by weight
ΣLi ₂ O+Na ₂ O+K ₂ O	3.8	to 5.5 per cent by weight
ΣCaO + BaO	1.0	to 2.5 per cent by weight
one or more refining agents	0.2	to 2.0 per cent by weight
and also one or more reducing agents	0.05	to 0.3 per cent by weight

2. A UV-transparent glass as claimed in claim 1, which has been produced using NaCl as refining agent.

3. A UV-transparent glass as claimed in claim 1 or 2, which has been produced using sugar as reducing agent.

4. A UV-transparent glass as claimed in claim 1 or 2, which has been produced using aluminum powder as reducing agent.



5. A UV-transparent glass as claimed in claim 1 substantially as described in Table 1.

6. A process for producing a UV-transparent glass as claimed in any one of claims 1 to 5 which comprises fusing a synthesis composition, calculated on an oxide basis of,

SiO ₂	64	to 66.5 per cent by weight
B ₂ O ₃	20	to 22.5 per cent by weight
Al ₂ O ₃	4	to 6 per cent by weight
Li ₂ O	0.4	to 1 per cent by weight
Na ₂ O	1.0	to 3.5 per cent by weight
K ₂ O	1.0	to 2.5 per cent by weight
CaO	0.35	to 0.8 per cent by weight
BaO	0.5	to 2.0 per cent by weight
F ⁻	0.5	to 2.0 per cent by weight
ΣLi ₂ O+Na ₂ O+K ₂ O	3.8	to 5.5 per cent by weight
ΣCaO + BaO	1.0	to 2.5 per cent by weight
one or more refining agents	0.2	to 2.0 per cent by weight
and also one or more reducing agents	0.05	to 0.3 per cent by weight

in a quartz crucible for 1.5 to 2.5 hours at 1500 to 1650°C and refining it for 2.5 to 4 hours at 1450 to 1600°C.

7. The use of a UV-transparent glass as claimed in any one of claims 1 to 5 or produced by a process as claimed in claim 6 for producing a UV lamp or a window glass of an EP-ROM.
