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JP 620187141 A **JP 600260443 A**

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(54) Abstract Title: **Colourless borosilicate glasses with special uv-edge**

(57) Borosilicate glass, having a spectral edge situation in the UV range of 280 to 325 nm, has the composition (in % by weight on an oxide basis)

SiO_2	60 - 75
B_2O_3	10 - 15
Na_2O	5 - 15
K_2O	5 - 10
Li_2O	0 - 5
CaO	0.1 - 1
BaO	0.5 - 3
TiO_2	>0 - 1.7
Sb_2O_3	0 - 0.5

and normal refining agents.

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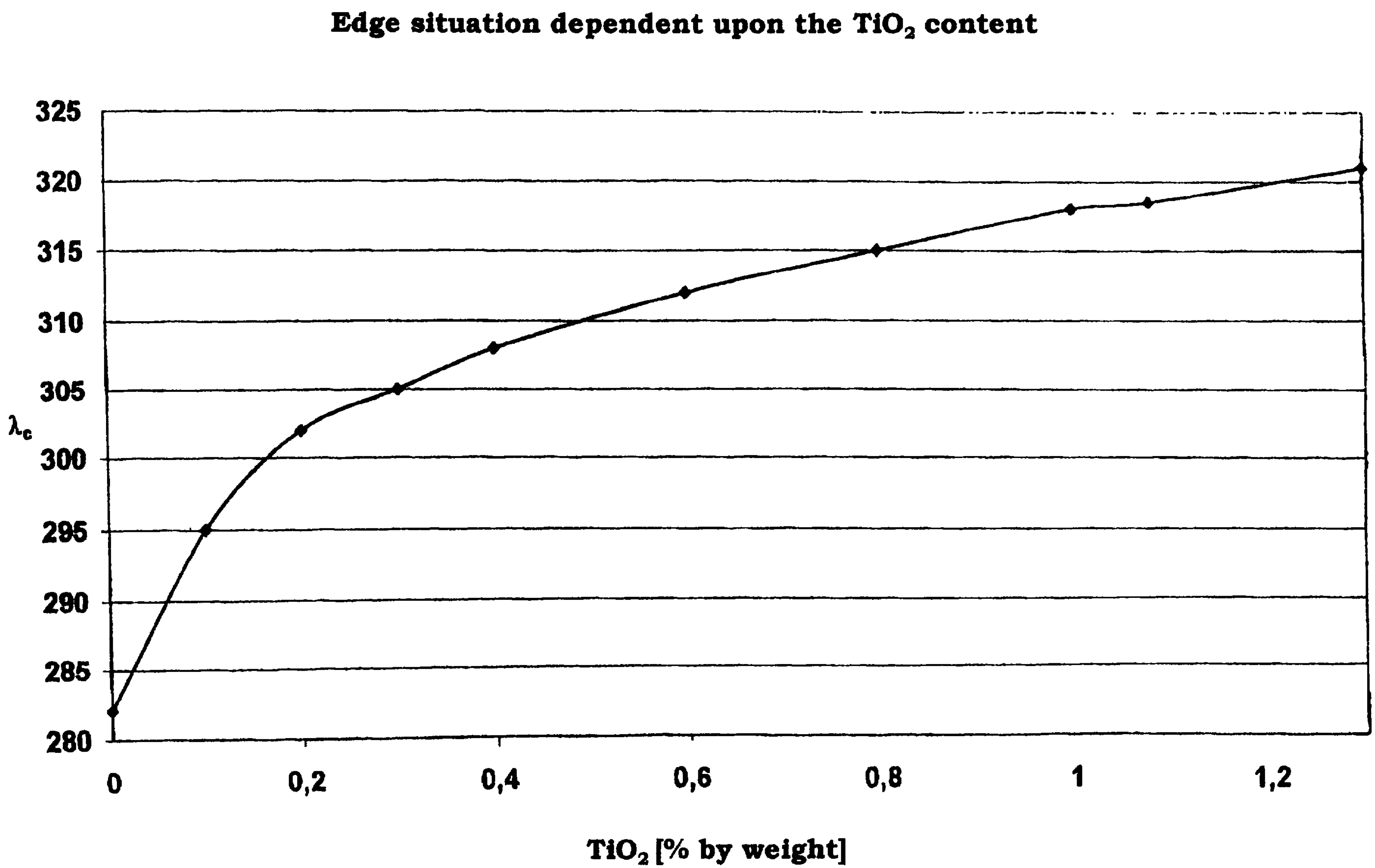
Edge situation dependent upon the TiO_2 content
λ_c
325
320
315
310
305
300
295
290
285
280
0
0,2
0,4
0,6
0,8
1
1,2
TiO_2 [% by weight]

Fig. 1

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Colourless glasses/borosilicate glasses with special UV-edge

The invention relates to a borosilicate glass with a special edge situation and the uses thereof.

In order to filter, in a targeted manner, a UV range which generally is defined as below 400 nm and can be divided into three sub-ranges, UVA, UVB and UVC, so-called colourless glasses or also optical glasses with defined edge situations are used. The edge situation or edge wavelength λ_c corresponds to half of the pure transmission maximum value between the blocking and permeable range.

A spectacle glass is known from EP 0 151 346 B1 which has a UV edge in the range between 325 nm and 335 nm. TiO_2 is added to the glass for this purpose. The proportion of TiO_2 is thereby 4 - 6 % by weight on an oxide basis.

This type of glass is not suitable for commercial application cases, in which a dimensional stability even at high transformation temperatures (for example > 560°C) and/or a stable expansion coefficient is required.

A stable expansion coefficient facilitates the incorporation or respectively exchange of the glasses in components.

The essential thing for the glasses in such technical applications is also their transmission course inclusive of UV edge. A defined steep UV edge is required in the UV range corresponding to the application purpose. For example, for illumination tables for burning-in phosphorus units into television screen units, UV radiation > 320 nm is required. For experiments with plants in plant cultivation, hard UV radiation > 280 nm is also definitely used. Weathering instruments for quality control change the UV ranges and hence filters according to each requirement.

JP 77 066 512 A describes UV filter glass with edge situations of approximately 370 nm made of a borosilicate glass which of necessity contains CeO_2 and otherwise in combination with TiO_2. The CeO_2 significantly increases the material costs in the glass. In addition, CeO_2 has a negative effect on the solarisation of the glass.

DE 639 456 A1 describes a lamp glass, made of a glass with a relatively wide composition range, in which SiO_2, B_2O_3 are components and Al_2O_3, MgO, CaO, BaO, BeO, Na_2O and K_2O can be contained. The glass claims no defined UV edge or optical situations.

GB 20 02 341 describes an optical fibre glass with a relatively wide composition range, in which SiO_2, B_2O_3 are components and Al_2O_3, MgO, CaO, BaO, SrO, Na_2O and K_2O can be contained. The glass likewise claims no defined UV edge, but rather glasses/fibres with refraction index gradients.

US 2,832,491 corresponds to a method patent, which is suitable for pre-loading of glass panes. The composition of the glass which is suitable for pre-loading contains in turn SiO_2 and B_2O_3 as components in a relatively wide range. Exact UV edges and optical situations cannot be set with this glass.

DE 195 32 800 A1 comprises the use of glasses for disinfection. A high transmission in the UVB and UVC range with reduced transmission in the visible and IR range is ensured by these glasses. This means that glasses with high transmission in the pass range are not possible.

DE 38 22 733 A1 describes solder glass made of a glass with a relatively wide composition range, in which SiO_2, B_2O_3 are components and Al_2O_3, MgO, CaO, BaO, SrO, ZnO, Li_2O, Na_2O and K_2O can be contained, at most 1% by weight alkali earth metal oxides being permitted to be contained. An alkali earth content of at least 1% by weight ensures a good chemical resistance, which permits the application of these filter glasses in a humid climate. The glass from DE 38 22 733 A1 does not make it possible to set a defined UV edge situation.

EP 0 505 061 A1 describes glass for protection covers for gallium arsenide solar cells with high UV absorption in the wavelength range of less than 320 nm. It contains SiO_2, B_2O_3, Na_2O, K_2O and CeO_2 as components. Al_2O_3, TiO_2, MgO, CaO, ZnO, SrO, BaO, PbO, Li_2O, As_2O_3, Sb_2O_3 and F are contained optionally. High UV transmissions are specifically avoided in the case of the described glasses.

EP 0 953 549 A1 describes glass for glass plates and substrates, which are used in electronics. The physical properties, such as expansion coefficient, the lower strain point, the density and the oxygen atom density are essential here. However, the UV edge situation or the optical properties are not relevant for these glasses.

It is the object of the invention to produce a UV permeable glass, the edge situation of which can be set in a defined and simple manner in the range between 280 and 325 nm, the glass being dimensionally stable at high operating temperatures and having a relatively constant expansion coefficient.

This object is achieved by a glass according to patent claim 1.

The borosilicate glass which is used fulfils the requirements in temperature and dimensional stability. The borosilicate glass can thereby be made available with a defined edge situation between 280 and 325 nm, with high transmission in the pass range, high optical density in the stop range and specific refraction indices and Abbé numbers. This is possible merely by varying the content of TiO_2 in the glass system.

The continuous production with edge situations λ_c of 280 to 325 nm is essential for these glasses. This continuous production is ensured because of the uniform base glass. TiO_2 is used as doping for the desired steep edge situation, an addition not being required in the case of very low edge situations < 290 nm. This type of production saves costs and time, i.e. it avoids long remelting phases, in which no usable glass is produced.

All the glasscs dcscribed here, apart from being used as colourless glass with specific edge situations, are used also as optical glasses with defined refraction indices n_d and dispersion v_d. As a result, uses in the field of imaging optics, projection, telecommunications, optical communications technology and microlithography are possible.

A glass with the desired optical and physical properties comprises preferably a basic glass system of 60 to 70% by weight SiO_2, 10 to 15% by weight B_2O_3, 5 to 15% by weight Na_2O, 5 to 10% by weight K_2O, 0.1 to 1% by weight CaO, 0.5 to 3 BaO and optionally 0 to 5% by weight Li_2O (preferably Li free), 0 to 2 TiO_2, 0 to 0.5% by weight Sb_2O_3 and normal refining agents.

The glass according to the invention contains SiO_2 in the % by weight range between 60 to 75, preferably 65 to 75% by weight and functions as glass former. Higher contents would impair the meltability, in the case of lower contents, would make the glass formation difficult. Lower SiO_2 proportions in the glass would also result in Abbé numbers which are too low.

B_2O_3 is a glass former exactly like SiO_2 and improves the meltability by reducing the viscosity. In the glass according to the invention, 5 to 15%

by weight B_2O_3, preferably 10 to 13% by weight, are contained. Lower contents than 5% by weight B_2O_3 would impair the meltability of the glasses, whereas higher contents than 15% by weight B_2O_3 impair the chemical resistance of the glass.

The contained alkali oxides Na_2O (5 to 15% by weight, preferably 6 to 12% by weight) and K_2O (5 to 10% by weight) serve to improve the meltability, i.e. to reduce the viscosity. In the case of alkali contents which are too high, above all the hydrolytic resistance would be impaired, but also to a lesser extent the resistance to alkali liquor. Above all, however, the Abbé number is reduced too greatly.

Of the alkali earth oxides, CaO with 0.1 to 1% by weight, preferably 0.1 to 0.5% by weight and BaO with 0.5 to 3% by weight, preferably 0.5 to 2.5% by weight, are contained in the glass according to the invention. The alkali earth oxides reduce the melt viscosity, repress the crystallisation and contribute to improving the resistance to alkali. CaO is therefore present in the glass at least with 0.1% by weight and BaO with at least 0.5% by weight. Both oxides are likewise indispensable for the setting of the optical situation. With higher contents, the Abbé number in turn could be reduced too greatly.

TiO_2 is required as an optional component for setting the UV situations greater than 280 nm. However more than 1.7% by weight of TiO_2 in the glass scarcely still effects a noticeable displacement of the UV edge in the longer-wave range in this glass system and promotes devitrification. In addition, too high contents of TiO_2, as indicated, would increase the refractive index too greatly and reduce the Abbé number too greatly.

The glass can be manufactured free of expensive CeO_2 apart from unavoidable impurities. This is advantageous for the steepness of the transmission curve during the transition from the stop to the pass range and for the solarisation resistance.

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The glass can in addition be free of PbO and of As_2O_3 apart from unavoidable impurities. The glass is thus free of toxic components and therefore ecologically harmless.

Sb_2O_3 is optionally a component and serves for use as refining agent. Nevertheless other normal refining agents are likewise possible.

Embodiment examples:

Normal optical raw materials are used for producing the exemplary glasscs.

The well homogenised glass batch was melted, refined and homogenised in the laboratory in a Pt crucible at 1420°C. Subsequently the glass was cast and cooled at 20 K/h.

Table 1 shows a melt example of a 0.5 l melt:

Oxides	% by weight		Raw material	Initial weight (g)
SiO_2	69.98		SiO_2	772.65
B_2O_3	11.19		H_3BO_3	219.5
Na_2O	9.49		$NaNO_3$	287.79
K_2O	7.29	3.8	K_2CO_3	61.69
		3.49	KNO_3	82.78
CaO	0.2		$CaCO_3$	3.94
BaO	1.35		$Ba(NO_3)_2$	25.38
TiO_2	0.20		TiO_2	2.22
Sb_2O_3	0.30		Sb_2O_3	3.31

The properties of the thus obtained glass are indicated in Table 2, Example 3.

Table 2 shows 9 examples of glasses according to the invention (1 to 9) with their compositions (in % by weight on an oxide basis) and their essential properties:

Example no.

Oxides	1	2	3	4	5	6	7	8	9
B_2O_3	11.21	11.20	11.19	11.18	11.17	11.15	11.12	11.10	11.07
BaO	1.35	1.35	1.35	1.35	1.35	1.34	1.34	1.34	1.34
CaO	0.20	0.20	0.2	0.20	0.20	0.20	0.20	0.20	0.20
K_2O	7.31	7.30	7.29	7.28	7.28	7.26	7.25	7.23	7.21
Na_2O	9.51	9.50	9.49	9.48	9.47	9.45	9.43	9.41	9.39
Sb_2O_3	0.28	0.30	0.3	0.30	0.30	0.30	0.30	0.30	0.30
SiO_2	70.13	70.05	69.98	69.91	69.84	69.70	69.56	69.42	69.21
TiO_2	0.01	0.10	0.20	0.30	0.40	0.60	0.80	1.00	1.30
Properties									
λ_c (d = 2 mm) [nm]	283	295	302	304	308	312	315	318	320
n_d (20 K/h)	1.51423	1.51474	1.51527	1.51566	1.51633	1.51718	1.51805	1.51986	1.52056
ν_d (20 K/h)	64.32	64.15	63.90	63.69	63.48	63.01	62.60	62.03	61.58
$\alpha_{(20/300°C)}$ [10^{-6}/K]	8.2	8.2	8.1	8.2	8.2	8.1	8.1	8.1	8.1
Tg[°C]	571	573	570	572	575	568	567	578	578

The edge situation, dependent upon the TiO_2 content, for a given glass composition is plotted in Fig. 1. As is evident therefrom, the edge situation can be set in a targeted and reproducible manner as a result of the dosed addition of TiO_2.

CLAIMS

1. Borosilicate glass with the composition (in % by weight on an oxide basis) of

SiO_2	60 - 75
B_2O_3	10 - 15
Na_2O	5 - 15
K_2O	5 - 10
CaO	0.1 - 1
BaO	0.5 - 3
TiO_2	> 0 - 1.7
Sb_2O_3	0 - 0.5

and normal refining agents.

2. Borosilicate glass according to claim 1,
characterised by
a composition (in % by weight on an oxide basis) of

SiO_2	65 - 75
B_2O_3	10 - 13
Na_2O	6 - 12
K_2O	5 - 10
CaO	0.1 - 0.5
BaO	0.5 - 2.5
TiO_2	0 - 1.7
Sb_2O_3	0 - 0.5

and normal refining agents.

3. Borosilicate glass according to at least one of the claims 1 to 2,
characterised in that
it contains in addition (in % by weight on an oxide basis):

SrO	0.5 - 2.5
Mg	0.1 - 1
Li_2O	0 - 5.

4. Borosilicate glass according to at least one of the claims 1 to 3, characterised in that it is free of As_2O_3, PbO and CeO_2 apart from unavoidable impurities.

5. Borosilicate glass according to at least one of the claims 1 to 4 with steep edge situations λ_c between 280 nm and 325 nm and a pure transmission degree of τ_{ip} in the pass range of > 98% and an optical density in the stop range of 1 * 10^{-5} with sample thickness of 2 mm.

6. Borosilicate glass according to one of the claims 1 to 5, characterised in that, with an edge situation in the range between 280 to 295 nm, it has a TiO_2 content of > 0 to 0.1% by weight on an oxide basis .

7. Borosilicate glass according to one of the claims 1 to 5, characterised in that, with an edge situation in the range between 290 and 305 nm, it has a TiO_2 content of 0.05 to 0.3% by weight on an oxide basis.

8. Borosilicate glass according to one of the claims 1 to 5, characterised in that, with an edge situation in the range between 300 to 315 nm, it has a TiO_2 content of 0.16 to 0.8% by weight on an oxide basis.

9. Borosilicate glass according to one of the claims 1 to 5, characterised in that, with an edge situation in the range between 310 to 325 nm, it has a TiO_2 content of 0.5 to 1.7% by weight on an oxide basis.

10. Use of a glass according to at least one of the claims 1 to 9, for the production of filter glass for UV cut-off filters in the UVB and/or UVC range.

11. Use of a glass according to at least one of the claims 1 to 10, for the production of filter glass for illumination tables or weathering instruments.

12. Use of a glass according to at least one of the claims 1 to 10, for the production of optical glass for imaging optics, projection, telecommunications, optical telecommunications technology and microlithography.

13. Borosilicate glass according to at least one of the claims 1 to 12, with a transformation temperature Tg > 560°C, with a thermal expansion coefficient $\alpha_{(20/300)}$ between 7.5 and 8.8 10^{-6}/K, steep edge situations between 275 nm and 325 nm.

The Patent Office

INVESTOR IN PEOPLE

Application No: GB 0322091.0 13 **Examiner:** Colin Clarke

Claims searched: 1-13 **Date of search:** 28 January 2004

Patents Act 1977 : Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X	1,2,4 at least	JP 60-260443 A NIPPON GLASS see example 2,5,6,9
X	1 at least	JP 62-187141 A NIPPON GLASS see examples 1 & 9

Categories

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art
Y	Document indicating lack of inventive step if combined with one or more other documents of same category	P	Document published on or after the declared priority date but before the filing date of this invention
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC[W]

C1M

Worldwide search of patent documents classified in the following areas of the IPC[7]

C03C

The following online and other databases have been used in the preparation of this search report

WPI, EPODOC, JAPIO