(12) UK Patent Application (19) GB (11) 2 137 981 A

(43) Application published 17 Oct 1984

(21) Application No 8405441

(22) Date of filing 1 Mar 1984

(30) Priority data

(31) 3307497 (32) 3 Mar 1983 (33) DE

(71) Applicant
Carl Zeiss Stiftung, (FR Germany),
Schott-Glaswerke, Hattenbergstr 10, 6500 Mainz,
Federal Republic of Germany

(72) Inventors
Danau Grabowski, Volkmar Geiler,
Dr. Ludwig Ross, Dr. Georg Gliemeroth

(74) Agent and/or address for service
Marks & Clerk, Alpha Tower, Suffolk Street
Queensway, Birmingham B1 1TT

(51) INT CL³
C03C 3/14

(52) Domestic classification
C1M 103 120 128 133 134 140 141 144 146 149 150 155 157 159 160 161 162 163 171 175 179 212 AG
U1S 3009 3072 3073 3074 C1M

(56) Documents cited
GB A 2024804 GB 1286749
GB 1562130

(58) Field of search
C1M

(54) Optical Glass

(57) Optical glass with nd≥1.70, vd≥48, having good stability to devitrification and good chemical resistance, has the following composition (in wt%):

SiO_2	0.5—10	$SiO_2+B_2O_3$=20—43
B_2O_3	15—35	
La_2O_3	35—51	
ZnO	0.5—10	
ZrO_2	2—8	
F^-	0.5—5	
M_2O	0—2.5	
AO	0—4.5	

Wherein M=Li, Na, K: A=Mg, Ca, Sr, Ba.
The glass may also comprise:

Y_2O_3	2—12	
Gd_2O_3	3—12	
CeO_2	0—1	CeO_2+SnO_2=0=2.1
SnO_2	0—1.6	
Nb_2O_5	0—3	
As_2O_3	0.1—1	

GB 2 137 981 A

SPECIFICATION
Optical Glass

It is an object of the present invention to provide a range of compositions for an optical glass having a refractive index of greater than or equal to 1.70 and an Abbe index of greater than or equal to 48, whose stability to devitrification is such that it is possible to produce large castings in high production numbers while meeting the customary optical quality requirements.

It has been proposed to introduce fluoride ions into glass, as described in DE—OS 27 56 160. These glasses contain, however, more than 17% (by weight) Gd_2O_3 and the stability to devitrification is very low in these glasses. DE—AS 26 33 946 describes glasses containing fluoride which are composed on the basis of B_2O_3—La_2O_3—Y_2O_3; these glasses, however, need to contain Ta_2O_5 which is very expensive.

The glasses described in JP—OS 78 04 023 partly overlap the position range in the nd-vd-diagram of the present application but these glasses by needs contain HfO_2 in amounts ranging as high as 25% by weight. Although the glasses described in DE—OS 31 380 138 contain from 1 to 4% F^- ions, they differ from the present application by having a content of WO_3 in amounts up to 20%.

A glass satisfying all requirements mentioned (good stability to devitrification, high refractive index with dispersion being as low as possible, absence of materials causing internal stresses in the glass such as Cd, Th) can be achieved using glass compositions according to the present invention.

According to the present invention there is provided an optical glass with a refractive index of greater than or equal to 1.70 and an Abbe index greater than or equal to 48, having the following composition (in % by weight):

SiO_2	0.5—10
B_2O_3	15 —35
La_2O_3	35 —51
ZnO	0.5—10
ZrO_2	2 — 8
F^-	0.5— 5
M_2O	0 — 2.5
AO	0 — 4.5

wherein M_2O is an alkali metal oxide or a mixture of alkali metal oxides, said alkali metal or metals being selected from Li, Na and K; AO is an alkaline earth metal oxide or mixture of alkaline earth metal oxides, said alkaline earth metal or metals being selected from Mg, Ca, Sr and Ba; and $SiO_2+B_2O_3$ falls in the range 20—43 weight %.

It is preferred that the optical glass of the present invention has the following composition:—

SiO_2	1 — 8
B_2O_3	26 —35
Na_2O	0.3— 1.5
K_2O	0.2— 2
Li_2O	0 — 1
ZnO	0.5— 6
CaO	0.5— 2
La_2O_3	39 —46
ZrO_2	2 — 8
Y_2O_3	2 —12
Gd_2O_3	3 —12
F^-	0.5— 5.

The M_2O content may be 0.5 to 2.5 or 0.2 to 2 (in percent by weight). It is preferred that as further components the glass contains 0—1 weight % CeO_2 and optionally SnO_2 such that CeO_2+SnO_2 is 0—2 weight %. As another component, 0—3 weight % Nb_2O_5 may be included.

In the glass according to the present invention, 0.5—5% by weight of the oxygen ions are replaced by fluoride ions. The fluoride ions, in addition to retarding crystallization and improving the melting properties of the mixture, cause an improvement in the transmission and a shift of the absorption edge (border/boundary) toward shorter wavelengths. The fluoride ions may typically be introduced into the glass by means of LaF_3, YF_3, NaF or KF, for example.

The essential feature of the glasses of the present invention is that they are free from oxides of Cd and Th, which cause internal stresses and that 0.5 to 5% by weight of the amount of O^{2-} ions have been replaced by F^- ions. The glasses of the invention are characterized by good chemical stability and very good transmission in the visible region of the spectrum.

The glasses of the invention meet the requirement for good stability towards devitrification when produced according to the currently customary technical glass melting procedures and have refractive values of greater than or equal to 1.70 and Abbe indices of greater than or equal to 48, which clearly differentiates them from the alkali-free glasses described in the Japanese patent applications or patents 75 006 326; 760 175 70, 780 4023, 31 830 138. The essential characteristic is that all these requirements have been met without any addition of any environmentally stressful oxides, such as CdO and ThO_2. Good crystallization stability is obtained through specific quantities of SiO_2, B_2O_3, ZnO, ZrO_2, Y_2O_3, Nb_2O_5 and Gd_2O_3, as well as balanced additions of M_2O-oxides, CeO_2 (up to 0.5% by weight), SnO_2 (up to 1.6% by weight). Additionally, it is possible to forego the utilization of very expensive raw materials such as Ta_2O_5 so that the glasses of the invention have a markedly lower cost component for raw materials than previously-known glasses (DE—OS 22 37 259 and JP—OS 50 14 712: which specify at least 2% by weight of Ta_2O_5).

The components used result in an excellent transmission (pure transmission at 400 nm and 25 mm layer thickness greater than or equal to 0.941 in the glasses of the present invention; which transmission cannot be obtained with known glasses containing, among other ingredients, TiO_2 and/or PbO (DE—AS 2 652 747).

The Table below contains 12 examples of embodiments in the preferred composition range.

The glasses of the invention are produced as follows:

The raw materials (oxides and preferably carbonates and fluorides) are weighed; a clarifying agent, such as As_2O_3, is added in quantities of 0.1—1% by weight, and then the mixture is mixed well. The glass mixture is melted down in a Pt or ceramic crucible at about 1260—1300°C, is then purified and homogenized well by means of an agitator. At a casting temperature of 1090—1200°C, the glass is then processed to the desired dimensions.

Melting Example for 100 kg Calculated Glass

Oxide	% by weight	Raw Material	Quantity Weighed in (Kg)	
SiO_2	3.90	powdered quartz	3.91	
B_2O_3	34.40	H_3BO_3	60.94	
Li_2O	0.40	Li_2CO_3	1.00	
CaO	1.40	$CaCO_3$	2.49	
ZnO	5.40	ZnO	5.43	
La_2O_3	45.80	La_2O_3	42.07	
		LaF_3	4.03	
ZrO_2	7.00		7.02	
Nb_2O_5	1.70	Nb_2O_5	1.70	
			129.49	
As_2O_3	0.20	As_2O_3	0.20	clarifying agent mixture
			129.69	

The properties of this glass are listed in Example 6 in the Table below.

	1	2	3	4	5	6	7	8	9	10	11	12
SiO_2	4.92	1.94	7.35	2.35	2.09	3.90	4.94	3.94	0.94	3.94	3.94	2.40
B_2O_3	34.00	32.00	27.00	31.00	31.64	34.40	29.21	34.06	32.40	29.20	27.71	30.60
Li_2O		0.50				0.40	0.30	0.75	0.30	0.30	0.30	
Na_2O			0.24	1.14								
K_2O												1.50
CaO					0.20	1.40	1.40	1.51		1.40	1.40	0.25
ZnO	1.40	5.40	2.40	2.40	0.70	5.40	5.40	5.40	8.75	5.40	5.40	2.05
La_2O_3	42.30	50.31	39.00	43.23	39.24	45.80	44.00	42.50	48.61	44.00	44.00	45.50
Y_2O_3	7.00		7.63	7.63	11.90		2.00			2.00	3.00	5.30
Gd_2O_3	7.58		11.30	8.00	10.92		4.00	3.48		4.00	6.00	8.10
CeO_2				0.25								
SnO_2			0.30				0.50			1.55		
ZrO_2	2.50	7.15	4.75	4.00	3.11	7.00	7.05	7.05	7.15	7.05	7.05	4.30
Nb_2O_5		2.50				1.70	1.20	1.20	1.85	1.20	1.20	
As_2O_3	0.30	0.20	0.30		0.20	0.20	0.10	0.30	0.10	0.10	0.10	0.10
F^-	1.60	1.80	1.20	1.60	1.50	1.20	1.60	1.20	0.85	1.20	4.15	0.50
nd	1.7287	1.7652	1.7490	1.7546	1.7548	1.7455	1.7515	1.7379	1.7590	1.7600	1.7585	1.7503
vd	55.78	48.9	51.70	52.15	52.49	50.54	50.20	51.0	49.5	48.5	50.2	50.46

CLAIMS

1. An optical glass with a refractive index of greater than or equal to 1.70 and an Abbe index greater than or equal to 48, having the following composition (in % by weight):

SiO_2	0.5—10
B_2O_3	15 —35
La_2O_3	35 —51
ZnO	0.5—10
ZrO_2	2 — 8
F^-	0.5— 5
M_2O	0 — 2.5
AO	0 — 4.5

wherein M_2O is an alkali metal oxide or a mixture of alkali metal oxides, said alkali metal or metals being selected from Li, Na and K; AO is an alkaline earth metal oxide or mixture of alkaline earth metal oxides, said alkaline earth metal or metals being selected from Mg, Ca, Sr and Ba; and $SiO_2+B_2O_3$ falls in the range 20—43 weight %.

2. A glass as claimed in Claim 1 comprising (in % by weight):

SiO_2	1 — 8
B_2O_3	26 —35
Na_2O	0.3— 1.5
K_2O	0.2— 2
Li_2O	0 — 1
ZnO	0.5— 6
CaO	0.5— 2
La_2O_3	39 —46
ZrO_2	2 — 8
Y_2O_3	2 —12
Gd_2O_3	3 —12
F^-	0.5— 5.

wherein $SiO_2+B_2O_3$ falls in the range 27—43 weight % and $Na_2O+K_2O+Li_2O$ falls in the range 0.2—2.5 weight %.

3. A glass as claimed in claim 1 or 2, further containing 0.2—2 weight % M_2O.

4. A glass as claimed in claim 1 or 2, further containing 0.5—2.5 weight % M_2O.

5. A glass as claimed in any one of claims 1 to 4 containing 0—1 weight % CeO_2.

6. A glass as claimed in any preceding claim further containing 0—0.5 weight % CeO_2.

7. A glass as claimed in any preceding claim further containing 0—1.6 weight % SnO_2.

8. A glass as claimed in any one of the preceding claims containing 0—3 weight % Nb_2O_5.

9. A glass as claimed in any one of the preceding claims containing 0—2.1 weight % CeO_2+SnO_2.

10. A glass as claimed in any one of claims 1 to 8 containing 0—2 weight % CeO_2+SnO_2.

11. A glass as claimed in claim 1 substantially as hereinbefore described in any one of Examples 1 to 12.

Printed in the United Kingdom for Her Majesty's Stationery Office, Demand No. 8818935, 10/1984. Contractor's Code No. 6378.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.