



- 1 -
Lead-free and preferably arsenic-free
lanthanum heavy flint glasses

5



159159

Description

The present invention relates to lead-free and preferably also arsenic-free lanthanum heavy flint glasses with a refractive index n_d of $1.84 \leq n_d \leq 1.96$ and an Abbé number v_d of $27 \leq v_d \leq 36$, and to the use of these glasses.

Conventional optical glasses in the lanthanum-heavy flint range with a low Abbé number for the application areas of imaging, projection, telecommunications, optical communication technology and laser technology generally contain PbO , in order to achieve the desired optical properties, i.e. a refractive index n_d of $1.84 \leq n_d \leq 1.96$ and, in particular, the high dispersion, i.e. a low Abbé number v_d of $27 \leq v_d \leq 36$. However, PbO reduces the chemical resistance of these types of glass. Furthermore, materials with high chemical resistances are becoming increasingly important for use in high added value products. Moreover, As_2O_3 is often used as a refining agent. Since in recent years the glass components PbO and As_2O_3 have been regarded as environmentally harmful, most manufacturers of optical instruments and products tend preferably to use lead-free and arsenic-free glasses.

30

Known lead-free glass compositions with a high refractive index and a low Abbé number generally contain extremely large quantities of TiO_2 in a silicate matrix, which leads to glasses which are very highly susceptible to crystallization and are extremely difficult to process.

In addition, in terms of melting technology there have recently been reports of increased demand for "short"

glasses, i.e. for glasses whose viscosity varies extremely strongly with the temperature. During the manufacturing process, this characteristic has the advantage that the hot-shaping times, i.e. the mould-closed times, can be reduced. This firstly increases throughput and secondly protects the mould material, with the result that total production costs can be reduced considerably. Also, the more rapid cooling which is thereby made possible also allows glasses with a relatively strong tendency to crystallization to be processed, i.e. correspondingly longer glasses, and means that preliminary nucleation, which could cause problems in subsequent secondary hot-forming steps, is avoided.

Therefore, a composition range for short optical glasses which allows the desired optical properties with regard to n_d and v_d to be achieved even without it being necessary to use PbO and As_2O_3 , and furthermore with a reduced TiO_2 content, would be advantageous.

The glasses with similar optical positions or comparable chemical compositions which have hitherto been disclosed in the prior art have serious drawbacks, however.

For example, DE 691 356 (Eastman Kodak) describes silicate-free lanthanum borate glasses for achieving a similar optical position, namely a very high refractive index with an extremely low dispersion (i.e. a high Abbé number), but these glasses are at very great risk of crystallizing. Moreover, to stabilize these glasses it is preferable to introduce very expensive tantalum oxide (or optionally highly toxic thorium oxide or expensive tungsten oxide) as crystallization inhibitor. Furthermore, when SiO_2 is used without the addition of alkali metal oxides, opacification phenomena have been described, and consequently the use of silicate is obligatorily linked to the addition of alkali metals.

In a corresponding way to the document discussed above, JP 78-004023 A (Ohara) also describes glasses with an extremely low dispersion and very high refractive indices. The glasses described differ from the glasses described in DE 691 356 through the obligatory requirement that hafnium be used to stabilize the lanthanum borate matrix. However, on account of the difficulty of purifying raw materials, this component is extremely expensive. Moreover, it has a very high melting point (melting point 3050°C) compared to its more usual homologs TiO_2 (melting point 1560°C) and ZrO_2 (melting point 1700°C) with comparable physico-chemical characteristics. The result of this is that the melting process is made considerably more difficult by additions of hafnium oxide.

JP 84-050048 A (Ohara) must include silicate-containing (> 8% by weight) lanthanum borate glasses, without alkali metal oxides necessarily being added. Since the solubility of lanthanum oxide in a borosilicate matrix is significantly worse than in a pure borate matrix, the maximum amount of lanthanum which can be used in these glasses is limited. Therefore, the result is either glasses whose refractive indices are lower on account of lower La_2O_3 contents or whose crystallization resistance is adversely affected by the effect of further oxides increasing the refractive index.

DE 31 38 137 (SCHOTT GLAS) relates to glasses with an extremely low dispersion combined, at the same time, with high refractive indices. The stabilizing effect with respect to the tendency to crystallize caused by the use of silicate without alkali metals is achieved by adding large amounts of Nb_2O_5 ($\geq 15\%$ by weight). This patent differs from DE 691 356 through the use of silicate in the absence of alkali metals and tantalum. However, since Nb_2O_5 is a relatively expensive component, such high levels of Nb_2O_5 are not economical.

DE 10 47 994 (Izumitani et al.) deals with lanthanum borate glasses with particularly high borate contents ($\geq 20\%$ by weight). Although these have a positive influence on the solubility of the lanthanum and therefore reduce the tendency to crystallize when silicate is used at the same time, they reduce the maximum refractive indices which can be reached to below 1.87. Therefore, the glasses described in this document tend to be designed for moderate optical positions with good chemical resistance, high grinding hardnesses, i.e. good machining properties, and low crystallization, rather than to achieve high refractive indices, combined with a low dispersion.

Therefore, the object of the present invention was to provide lead-free and preferably also arsenic-free optical glasses for the application areas of imaging, projection, telecommunications, optical communication technology and/or laser technology with a refractive index n_d of $1.84 \leq n_d \leq 1.96$ and an Abbé number v_d of $27 \leq v_d \leq 36$ which have good melting and processing properties. Furthermore, these glasses are to have a good chemical resistance and sufficient crystallization resistance, so that they can be produced in continuously operated installations.

The above object is achieved by the embodiments of the present invention which are described in the claims.

In particular, the present invention relates to glasses with a refractive index n_d of $1.84 \leq n_d \leq 1.96$ and an Abbé number v_d of $27 \leq v_d \leq 36$ which are characterized by the following composition (in % by weight, based on oxide):

SiO ₂	1	-	8
B ₂ O ₃	13	-	19.5
La ₂ O ₃	34	-	50

	MgO	0	-	6
	CaO	0	-	6
	BaO	0	-	6
	ZnO	0	-	9
5	Σ MO	1	-	10
	TiO ₂	4	-	15
	ZrO ₂	0	-	11
	Nb ₂ O ₅	6	-	14.5

10 According to the present invention, the details given with regard to the weight of the components are in each case based on oxide unless stated otherwise.

15 The glasses according to the invention have the same optical data as known optical glasses of this optical position. However, they are also distinguished by good chemical resistance and processing properties, lower production costs on account of reduced raw material and process costs, crystallization resistance, which is
20 sufficient on account of the glasses being short, and by good environmental compatibility.

The glasses according to the invention satisfy both the requirement for good melting and processing properties,
25 with a refractive index n_d of $1.84 \leq n_d \leq 1.96$, preferably $1.85 \leq n_d \leq 1.95$, particularly preferably $1.86 \leq n_d \leq 1.94$, most preferably $1.88 \leq n_d \leq 1.93$, and an Abbé number v_d of $27 \leq v_d \leq 36$, preferably $28 \leq v_d \leq 35$, particularly preferably $28 \leq v_d \leq 34$, most
30 preferably $29 \leq v_d \leq 33$ and the requirement of having a good chemical resistance and resistance to crystallization, while at the same time not containing PbO and preferably also not containing any As₂O₃.

35 The basic glass system is a lanthanum borate glass, the borate being responsible for the solubility of the lanthanum. It has been found that stable glasses are formed at La₂O₃: B₂O₃ ratios of ≤ 3.0 . The range which is

preferred according to the invention starts at La_2O_3 : B_2O_3 ratios of around approximately 2.6. Although lower ratios are desirable with regard to the resistance to crystallization, they would require
5 significantly higher absolute borate contents, with the result that it would no longer be possible to introduce sufficient amounts of highly refractive components which do not promote crystallization to achieve the refractive index position which is desired in the
10 present context.

To achieve the desired optical position, the glass according to the invention contains an La_2O_3 content of at least 34% by weight, preferably at least 37% by
15 weight, more preferably at least 39% by weight, most preferably at least 40% by weight. The La_2O_3 content is at most 50% by weight, preferably at most 47% by weight, particularly preferably at most 45% by weight, most preferably at most 44% by weight.

20 According to the invention, the B_2O_3 content is preferably at least 13% by weight, preferably at least 15% by weight, more preferably at least 16% by weight, most preferably at least 17% by weight. The glass
25 according to the invention contains at most 19.5% by weight, preferably at most 19% by weight of B_2O_3 .

The glasses according to the invention are restricted to SiO_2 contents of at most 8% by weight, allowing up
30 to 50% by weight of lanthanum oxide to be used. Therefore, there is no need to add further components which increase the refractive index but promote crystallization in order to achieve the high refractive index positions.

35 Therefore, the glass according to the invention contains only small amounts of the glass former SiO_2 , i.e. at most 8% by weight, preferably at most 7.5% by weight, more preferably at most 7% by weight, most

preferably at most 6% by weight. However, the glass according to the invention always contains small quantities of SiO_2 , in an amount of at least 1% by weight, preferably at least 3% by weight particularly preferably at least 4% by weight. This low SiO_2 content is used to improve the processing properties by increasing the mechanical strength of the material. For example, good abrasion hardnesses and chemical resistances can be achieved as a function of the quantity used. However, the amount of SiO_2 added must be restricted to the upper limit described above, since otherwise the solubility of the lanthanum in the matrix is reduced. This in turn leads to glasses which lack resistance to crystallization or, if the La_2O_3 content has been reduced in favour of the SiO_2 content, to lower refractive indices and to shifts of the overall optical position.

The most important optical component of the glass according to the invention, i.e. the component which has a major influence on achieving the desired optical position with a high refractive index and a low Abbé number, is Nb_2O_5 . Further Nb_2O_5 stabilizes the silicate-containing lanthanum borate glass matrix. This component is present in an amount of at least 6% by weight, preferably at least 8% by weight, particularly preferably at least 9% by weight, most preferably at least 10% by weight, in the glass. This component is present in the glass according to the invention at most in an amount of 14.5% by weight, preferably 14% by weight, and particularly preferably 13% by weight. Increasing the amount of this component to above 14.5% by weight would lead to increased batch preparation costs. Furthermore, on account of the glass being short, there is no need to exploit the further stabilizing effect in the processes. Reducing the level of this component to below 6% by weight would increase the likelihood of crystallization to such an extent

that it would only be possible to obtain a glass with considerable difficulty.

5 The glass according to the invention is what is known as a "short glass"; this expression is understood as meaning that the viscosity of the glass drops relatively quickly as the temperature falls or increases relatively quickly as the temperature rises.

10 This "shortness" of the glass according to the invention is achieved by the combination of a defined quantity of TiO_2 with a defined quantity of one or more alkaline-earth metal oxides.

15 The amount of TiO_2 in the glass according to the invention is at most 15% by weight, preferably at most 13% by weight, particularly preferably at most 12% by weight, most preferably 11% by weight. Increasing the
20 TiO_2 content to over 15% by weight would firstly lead to the viscosity-temperature profile being made undesirably extreme, i.e. the glass would become so "short" that it would be difficult to process under standard conditions. Furthermore, such a high TiO_2 content would detrimentally lead to a considerable
25 increase in the tendency of the glass to crystallize. Therefore, according to preferred embodiments, TiO_2 may if appropriate be partially replaced by ZrO_2 (0 - 11% by weight, preferably 1 - 9% by weight, particularly preferably 2 - 9% by weight, most preferably 3 - 8% by
30 weight). Furthermore, TiO_2 contents of over 15% by weight result in an Abbé number which is too low for the desired application areas, i.e. in excessively high dispersion. The glass contains at least 4% by weight, preferably at least 6% by weight, particularly
35 preferably at least 7% by weight, most preferably 8% by weight, of this component. By contrast, reducing the content of this component to below 4% by weight would lead to there being insufficient amounts of this

component to obtain a sufficiently "short" glass, and the Abbé numbers would be too high.

According to the present invention, the glass according
5 to the invention also contains alkaline-earth metal
oxides. The use of the alkaline-earth metal oxides in
combination with the addition of TiO_2 serves to modify
the viscosity-temperature profile. Therefore, it is
possible to use any alkaline-earth metal oxide
10 individually or a mixture of two or more alkaline-earth
metal oxides within a wide range. However, the total
amount of alkaline-earth metal oxides must not exceed
an amount of 10% by weight, preferably 9% by weight. To
achieve the purpose of the invention, the glass
15 according to the invention contains at least 1% by
weight, preferably at least 2% by weight, of alkaline-
earth metal oxides.

However, since these components may also have an
20 influence on the optical position, MgO and CaO , as
components with a low refractive index, are only
present in the glass according to the invention in an
amount of in each case at most 6% by weight, preferably
in each case at most 4% by weight. Therefore,
25 particularly preferred variants of the glass according
to the invention are substantially free of these
components. Therefore, according to the present
invention, the alkaline-earth metal oxides contained in
the glass according to the invention are preferably the
30 components BaO and/or ZnO , which have a higher
refractive index. BaO is preferably present in an
amount of at most 6% by weight, preferably at most 4%
by weight, most preferably at most 3% by weight, in the
glass according to the invention. The glass according
35 to the invention preferably contains at least 1% by
weight of BaO . The glass according to the invention
contains ZnO in an amount of preferably at most 9% by
weight, for preference at most 7% by weight, most
preferably at most 6% by weight, and preferably in an

amount of at least 1% by weight. It has been found that in particular ZnO appears to act as a crystallization inhibitor. It is therefore particularly preferred to add at least one of these alkaline-earth metal components.

The glass according to the invention may also contain an addition of alkali metal oxides which, however, do not produce any stabilization of the glass in the small quantities which are the maximum permitted. However, adding larger amounts would lead to reductions in the refractive index. However, alkali metal oxides of this type may be necessary for certain applications, if glass properties such as, for example, an ion exchange capacity or slight variations to the viscosity-temperature profile towards flexible, near net shape hot forming are desired.

Therefore, in addition to the components mentioned above, the glasses according to the invention may if appropriate contain a total of at most 10% by weight, preferably at most 8% by weight, of alkali metal oxide (Na_2O , Li_2O , K_2O , and/or Cs_2O).

Furthermore, standard refining agents may also be present, but it is preferable for the refining agents used not to be arsenic compounds. In particular, the following components, individually or as a mixture, may be present as refining agents (in % by weight):

30	Sb_2O_3	0 - 1	and/or
	SnO	0 - 1	
	NaCl	0 - 1	
	SO_4^{2-}	0 - 1	
35	F^-	0 - 1	

According to a preferred embodiment, the glasses according to the invention are preferably also substantially free of arsenic and arsenic compounds.

- The glasses according to the invention, with a relatively moderate optical position with regard to the dispersion, are also sufficiently resistant to crystallization even when silicate is used (at most 8% by weight) without any addition of alkali metals. It is assumed that this is the case because of their "shortness". It is possible to dispense with expensive (or toxic) additions of Ta_2O_5 , WO_3 and/or thorium oxide; potentially inexpensive and ecologically harmless alkaline-earth metal oxides are used to stabilize the glasses according to the invention. Therefore, the glass according to the invention is preferably also free of Ta_2O_5 , WO_3 and/or thorium oxide.
- 15 The present invention also relates to the use of the glasses according to the invention for the application areas of imaging, projection, telecommunications, optical communications technology and/or laser technology.
- 20 Furthermore, the present invention relates to optical elements which comprise a glass according to the invention. Optical elements in this context may in particular be lenses and prisms, although they are not restricted to these particular examples. Furthermore,
- 25 the term "optical elements" also encompasses what are known as compact components.

Examples

- 30 The glasses according to the invention are produced in the following way:

The raw materials for the oxides, preferably carbonates, nitrates and/or fluorides, are weighed out, one or more refining agents, such as for example Sb_2O_3 , is/are added and the materials are then intimately mixed. The glass batch is melted at approx. $1300^\circ C$ in a continuous melting unit, then refined ($1350^\circ C$) and homogenized. The glass is cast at a casting temperature

of approximately 1220°C and processed into the desired dimensions.

Melting example of 100 kg (calculated) of glass
5 (Table 1)

Oxide	% by weight	Raw material	Amount weighed in (kg)
SiO ₂	3.0	SiO ₂	3.00
B ₂ O ₃	20.0	H ₃ BO ₃	35.53
La ₂ O ₃	46.7	La ₂ O ₃	46.70
ZnO	6.0	ZnO	6.00
BaO	0.2	Ba(NO ₃) ₂	0.34
BaO	3.8	BaCO ₃	4.89
TiO ₂	8.0	TiO ₂	8.00
Nb ₂ O ₅	12.0	Nb ₂ O ₅	12.00
Sb ₂ O ₃	0.3	Sb ₂ O ₃	0.30
Total	100.0		116.76

The properties of the glass obtained in this way are given in Table 2, Example 3.

10

Table 2 includes Examples 1 to 7 according to the invention and optical properties measured on the glasses.

15 The glasses according to the invention presented by Examples 1 to 7 (Table 2) set the crystallization resistance and viscosity-temperature profile in such a manner that further heat treatment (extrusion or repressing) of the glasses is readily possible.

20

In Comparative Example 1, which is not covered by the composition range according to the invention, the desired optical position can only be achieved by adding a considerable amount of expensive Nb₂O₅.

Table 2 Melting Examples (in % by weight)

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Comparative Example 1
	17181	17182	17183	17184	17185	17187	16250	15988
SiO ₂	4.0	8.0	3.0	5.0	6.0	4.0	6.0	3.0
B ₂ O ₃	16.0	20.0	20.0	19.0	15.0	19.0	18.0	21.0
La ₂ O ₃	41.0	37.0	47.0	45.0	39.0	44.0	41.0	50.0
Na ₂ O				3.0	2.0			
MgO		2.0			2.0	4.0		
CaO	2.0				2.0	4.0		
BaO		4.0	4.0	2.0	4.0		2.0	
ZnO	7.0		6.0	6.0	4.0	1.0	5.0	
TiO ₂	13.0	6.0	8.0	10.0	8.0	9.0	9.0	4.0
ZrO ₂	7.0	9.0		2.0	6.0	5.0	6.0	5.0
Nb ₂ O ₅	10.0	14.0	12.0	8.0	12.0	10.0	13.0	17.0
Sb ₂ O ₃	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Total	100.3	100.3	100.3	100.3	100.3	100.3	100.3	100.3
n _d	1.9448	1.9064	1.8908	1.8583	1.8772	1.8774	1.9144	1.9054
v _d	29.25	30.27	32.92	33.04	32.75	33.62	31.61	33.07
P _{G,F}	0.6008	0.5845	0.5907	0.5905	0.5916	0.5882	0.5937	0.5888
ΔP _{G,F} (10 ⁻⁴)	62	42	23	23	29	9	31	6
ρ (g/cm ³)	4.54	4.18	4.56	4.32	4.38	4.31	4.49	4.58
α ₂₀₋₃₀₀ (10 ⁻⁶ * K ⁻¹)	7.6	7.0	7.7	8.4	8.5	8.2	7.2	7.2
Tg (°C)	640	660	636	591	616	650	645	660

5

Claims

1. Lead-free optical glass with a refractive index n_d of $1.84 \leq n_d \leq 1.96$ and an Abbé number v_d of $27 \leq v_d \leq 36$, characterized in that it comprises the following composition (in % by weight based on oxide):

	SiO ₂	1	-	8
	B ₂ O ₃	13	-	19.5
15	La ₂ O ₃	34	-	50
	MgO	0	-	6
	CaO	0	-	6
	BaO	0	-	6
	ZnO	0	-	9
20	Σ MO (MgO, CaO, BaO, ZnO)	1	-	10
	TiO ₂	4	-	15
	ZrO ₂	0	-	11
	Nb ₂ O ₅	6	-	14.5

2. Lead-free optical glass according to Claim 1, having a refractive index n_d of $1.85 \leq n_d \leq 1.95$ and an Abbé number v_d of $28 \leq v_d \leq 35$, characterized in that it comprises the following composition (in % by weight based on oxide):

	SiO ₂	3	-	7.5
	B ₂ O ₃	15	-	19.5
	La ₂ O ₃	37	-	47
	MgO	0	-	4
35	CaO	0	-	4
	BaO	0	-	4
	ZnO	0	-	7
	Σ MO (MgO, CaO, BaO, ZnO)	2	-	10

TiO ₂	6	-	13
ZrO ₂	1	-	9
Nb ₂ O ₅	8	-	14

- 5 3. Lead-free optical glass according to Claim 1 or 2, having a refractive index of $1.86 \leq n_d \leq 1.94$ and an Abbé number of $28 \leq v_d \leq 34$, characterized in that it comprises the following composition (in % by weight, based on oxide):

10

SiO ₂	4 - 7
B ₂ O ₃	16 - 19.5
La ₂ O ₃	39 - 45
MgO	0 - 4
CaO	0 - 4
BaO	1 - 4
ZnO	1 - 7
Σ MO (MgO, CaO, BaO, ZnO)	2 - 9
TiO ₂	7 - 12
ZrO ₂	2 - 9
Nb ₂ O ₅	9 - 13

15

20

4. Lead-free optical glass according to one of Claims 1 to 3, having a refractive index n_d of $1.88 \leq n_d \leq 1.93$ and an Abbé number v_d of $29 \leq v_d \leq 33$, characterized in that it comprises the following composition (% by weight, based on oxide):

30

SiO ₂	4 - 6
B ₂ O ₃	17 - 19
La ₂ O ₃	40 - 44
BaO	1 - 3
ZnO	1 - 6
TiO ₂	7 - 11
ZrO ₂	3 - 8
Nb ₂ O ₅	10 - 13

35

5. Glass according to one of Claims 1 to 4, also containing a total alkali metal oxide content (Na_2O , Li_2O , K_2O , Cs_2O) of at most 10% by weight.
- 5 6. Glass according to one of Claims 1 to 5, also containing, as refining agent, one or more of the following components (in % by weight):
- | | | | |
|----|-------------------------|-------|--------|
| 10 | Sb_2O_3 | 0 - 1 | and/or |
| | SnO | 0 - 1 | |
| | NaCl | 0 - 1 | |
| | SO_4^{2-} | 0 - 1 | |
| | F^- | 0 - 1 | |
- 15 7. The use of a glass according to one of Claims 1 to 6 for the application areas of imaging, projection, telecommunications, optical communication technology and/or laser technology.
- 20 8. Optical element comprising a glass according to one of Claims 1 to 6.