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(71) Applicant: SCHOTT AG [DE/DE]; Hattenbergstraße 10, 55122 Mainz (DE).

(72) Inventors: FOTHERINGHAM, Ulrich; c/o SCHOTT AG, Hattenbergstrasse 10, 55122 Mainz (DE). LETZ, Martin; c/o SCHOTT AG, Hattenbergstrasse 10, 55122 Mainz (DE). THOMAS, Jens Ulrich; c/o SCHOTT AG, Hattenbergstrasse 10, 55122 Mainz (DE). SCHREDER, Bianca; c/o SCHOTT AG, Hattenbergstrasse 10, 55122 Mainz (DE). WEGENER, Holger; c/o SCHOTT AG, Hattenbergstrasse 10, 31073 Grünenplan (DE).

(74) Agent: SCHOTT CORPORATE IP; c/o SCHOTT AG Hattenbergstraße 10, 55122 Mainz (DE).

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(54) Title: GLASSES FOR LOCAL INDEX MODIFICATION BY ULTRASHORT PULSE LASER TREATMENT AND DEVICES COMPRISING THE SAME

(57) Abstract: The invention provides a glass or a glass substrate with constituent phases which enable the inscription of waveguides by usp-lasers, wherein the thermal expansion coefficient is at most 8ppm/K, especially from 2.5ppm/K to 8ppm/K. The glass therefore is especially suitable for the combination with semiconductor devices or substrates, e.g. for the production of an electronic or optoelectronic devices.

WO 2025/131402 A1

Glasses for Local Index Modification by Ultrashort pulse Laser Treatment and Devices comprising the same

The invention refers to glasses which combine suitability for local index modification by ultrashort pulse laser (usp-laser) treatment with a low thermal expansion, advantageously matching especially to that of semiconductor materials such as silicon, i.e. a comparatively low thermal expansion coefficient (CTE), and devices incorporating those glasses, especially devices comprising the glass and a semiconductor element.

State of the Art

US 7262144 B2, published 28 August 2007, teaches glasses particularly suitable for photo structuring. Essentially, these are Lithium-Aluminium Silicate (LAS) glasses with minor contributions of other atoms.

The usp-laser treatment will lead, first, to a local melting of the glass in the focal area of the laser, and, second, to a high temperature gradient there. According to Shimizu et al., this temperature gradient will give rise to a Soret effect with the heavier ions accumulating in the colder areas and the lighter ones accumulating in the hotter area. This effect makes LAS systems particularly suited for increasing the refractive index that way. Aluminium is lighter than Silicon, Lithium is even very much lighter than Silicon so that a LAS system will separate into a Lithium- and Aluminium-rich zone in the centre of the focal area and a Lithium- and Aluminium-deprived area around it.

The impact on the refractive index can be assessed considering the polarizability of the ions. Both for Lithium and Aluminium, the polarizabilities given there are bigger than the ones of Silicon.

In the light of the Soret effect, further light components such as Sodium or Magnesium may be favourable for a glass suitable for usp-laser-structuring. The difference

in weight to Silicon is much smaller for them than it is for Lithium; on the other hand, however, the polarizabilities are much higher. US 7262144 B2 contains both Sodium and Magnesium as components. On the contrary, US 7262144 B2 discloses the avoidance of Boron by introducing an upper limit for it. Because of its atomic weight, Boron will accumulate in the centre of the focus, which is not desirable, however, with respect to its ultra-low polarizability. Further components mentioned in US 7262144 B2 like Potassium and Zinc do not contribute to the refractive index in the desired way but are there in order to, e.g., suppress devitrification and to enhance meltability.

To combine the glasses taught by US 7262144 B2 with semiconductor materials, it has to be ensured that the thermal expansion coefficient does not exceed certain values. As both, the suitability for usp-laser-structuring and the thermal expansion coefficient have the tendency to rise with rising Lithium content, such glasses usually have high coefficients of thermal expansion. This is advantageous for the meltability because the temperature range, at which the viscosity of the glass is low enough for melting and hotforming, inversely scales with the thermal expansion. It is disadvantageous for combining with semiconductor materials the thermal expansion coefficients of which are usually significantly lower.

Object

In the state of the art, there is a lack of glasses that combine suitability for local index modification by usp-laser treatment with an advantageous thermal expansion and a rational meltability. In addition, it should be advantageous to manufacture the glasses using modern flat glass production methods.

The goal of the present invention is therefore to provide glass substrates, which are suitable for the following process: by moving the focus of an ultrashort pulse laser through the glass, permanent lines of modifications can be realized within the glass substrate volume, without modifying the volume surrounding the modification line. Depending on the laser focus intensity and material thresholds, the material

modification of the line can consist of micro voids, optical damages, birefringent nanovoids or density changes that result in a locally higher refractive index.. The later modification, the raise of the refractive index is favorable in the context of this invention, because the modification lines can then serve as waveguide cores. The flexibility of "writing" the modification lines freely within the glass substrate volume enables complex 3-dimensional waveguide circuits. Evanescent coupling between waveguides can be achieved to place waveguide cores in close vicinity (so that the evanescent parts of the waveguide modes overlap). Based on this principle coupling from one to N waveguides, therefore waveguide splitters can be achieved. They may optionally be combined by optical elements which may also be generated by a usp-laser, e.g., diffractive optical structures which serve as filters or in-line reflectors (Bragg-Gratings). Also, the modification lines itself can have a sub-structure, e.g. a periodic or an-periodic modulation along the line or a modification profile across the transversal cross-section.

The object is solved by the subject-matter of the independent claims. Preferred embodiments can be derived from the dependent claims.

Description of the invention

The object is solved by a specific combination of stoichiometric glasses, i.e. glasses which exist in the same stoichiometry also as crystals and whose properties can be assumed to be very similar for both glass and crystal because of the identical topology of the assemblies. This theorem can be verified in the literature in many examples by NMR measurements or the like. For this purpose, such stoichiometric glasses are selected whose mixture provide a behavior in the sense of a solution of the object according to the invention attainable. In the present invention, these stoichiometric glasses are also referred to as "constituent phases".

The concept to describe glasses on the basis of the constituent phases to be assigned to them has been applied before. By specifying the constituent phases, conclusions can be drawn about the chemical structure of a glass (see Conradt R:

"Chemical structure, medium range order, and crystalline reference state of multicomponent oxide liquids and glasses", in Journal of Non-Crystalline Solids, Volumes 345-346, 15 October 2004, Pages 16-23).

In one aspect, the invention relates to a glass having the following combination of constituent phases:

Table 1

Constituent Phase	min	max
Lithium-Disilicate	10	100
Spodumene	0	40
Albite	0	20
Orthoklas	0	20
Disodiumzincosilicate	0	20
Cordierite	0	20
Silicon Dioxide	0	50
Diboron Trioxide	0	5
Magnesiummetaphosphate	0	40

The composition is chosen with regard to the phases constituting the glass within the limits described herein. The phases constituting the glass are, of course, not present as such in the glass product in crystalline, but amorphous form. This does not mean, however, that the constituent phases have completely different building units in the amorphous state than in the crystalline state. As stated above, the topology of the building units is comparable, e.g., the coordination of the cations involved

with surrounding oxygen atoms or the interatomic distance resulting from the coordination and the strength of the bond between these cations and surrounding oxygen atoms. Therefore, many properties of the glass of the invention can be well described on the basis of the constituent phases, in particular to illustrate the inventive achievement and the problems overcome by the invention. Of course, the glass can be produced not only by using the corresponding crystals, but also by using the usual glass raw materials, as long as only the stoichiometric ratios allow the formation of the corresponding building blocks of the constituent phases.

Suitability for local index modification by usp-laser

The suitability for local index modification by usp-laser treatment is made sure by the above upper limits for the content of heavy ions (e.g. Potassium, Zinc) containing constituent phases.

Coefficient of thermal expansion according to ISO 7991

Surprisingly, the position of the thermal expansion coefficient according to ISO 7991 in the target range can also be represented with the aid of a calculation rule taking into account the average bond strength.

It is known in the art that the coefficient of thermal expansion for metals, for example, is inversely proportional to the binding energy (or to the "depth of the interatomic potential wells").

In an abstract picture of oxidic glasses, the cations are placed in a potential well formed by the surrounding oxygen atoms and the depth of the potential well is assumed to be the sum of the bond strengths of the various single bonds to the surrounding oxygen atoms, i.e. the entire interaction energy is concentrated in potential wells with the cations in the center and the oxygen atoms in the periphery. Thus, the reverse case needs no longer be considered; it would also be more difficult to ana-

lyze, since an oxygen atom can be located between several different types of cations, which conversely cannot occur in purely oxide glasses. These values are tabulated, e.g. in DE 10 2014 119 594 A1:

Table 2

Cation	Potential well depth / (kJ/mol)
Si	1864
B	1572.5
Al	1537
Zn	728
Mg	999
Li	585
Na	440.5
K	395
P	1691.5

The values which are not taken from DE 10 2014 119 594 A1 have been calculated using exactly the same method described there from the values given in Standard Thermodynamic Values at 25°C, retrieved from the literature.

From the composition of a glass comprising or consisting of the constituent phases given above, the numbers of different cations contained in the respective phases,

and the potential well depths per cation tabulated above, a mean potential well depth $\overline{E_{pot}}$ can be calculated:

$$\overline{E_{pot}} = \frac{\sum_{i=1}^n c_i \cdot \sum_{j=1}^m z_{i,j} \cdot E_{pot,j}}{\sum_{i=1}^n c_i \cdot \sum_{j=1}^m z_{i,j}}, \quad (1)$$

Where m is the number of cation types occurring in each constituent phase (the numerical value of m depends on the constituent phase), $E_{pot,j}$ is the potential well depth tabulated above for the j-th cation type, and $z_{i,j}$ is the number of cations of the j-th type in the i-th constituent phase. The sums over j are tabulated below:

Table 3

Constituent Phase	$\sum_{j=1}^m z_{i,j}$	$\sum_{j=1}^m z_{i,j} \cdot E_{pot,j} / \left(\frac{\text{kJ}}{\text{mol}} \right)$
Lithium-Disilicate	1.33	1632.67
Spodumene	1.33	1950
Albite	1.25	1892.38
Orthoklas	1.25	1881
Disodiumzincosilicate	1.2	1440.2
Cordierite	1.22	1940.67
Silicon Dioxide	1.00	1864
Diboron Trioxide	2.00	3145
Magnesiummetaphosphate	1.5	2191

This average bond strength is inversely proportional to the coefficient of thermal expansion, as is the case for metals. Evaluation of a number of different glasses, including commercial glasses such as Borofloat33, Borofloat40, AF45, AF32 leads to the following formula:

$$CTE = \frac{\left(\frac{51815 \left(\frac{kJ}{Mol} \right)}{E_{pot}} - 27.205 \right) ppm}{K}, \quad (2)$$

Since the bond strength is inversely proportional to the melting point, an inverse proportionality also applies between the melting point and the coefficient of expansion. Since the melting point is not precisely defined for non-stoichiometric glasses, only a tendential relationship applies between a typical temperature for the melting and hot forming range, e.g., the working point, at which the viscosity is 10^4 dPa·s, and the coefficient of expansion. However, this tendential relationship makes it clear that the combination of low coefficient of thermal expansion and an upper limit for the working point is challenging, especially if the glass is simultaneously supposed to have a high lithium fraction, which favours a low working point but does not favour a low coefficient of thermal expansion.

With respect to the interferometric effects, coupling of neighbouring structures etc. the thermal expansion coefficient of the glass should be made small, preferably as close as possible to the one of silicon in order to suppress any negative effect caused by an expansion mismatch. Therefore, the thermal expansion coefficient (CTE) of the glass is preferred to be at most 8 ppm/K, more preferably at most 7.75 ppm/K, more preferably at most 7.5 ppm/K, more preferably at most 7.25 ppm/K, more preferably at most 7 ppm/K, more preferably at most 6.75 ppm/K, more preferably at most 6.5 ppm/K, more preferably at most 6.25 ppm/K, more preferably at most 6.0 ppm/K, more preferably at most 5.75 ppm/K, more preferably at most 5.5 ppm/K, more preferably at most 5.25 ppm/K, more preferably at most 5.0 ppm/K, more preferably at most 4.75 ppm/K, more preferably at most 4.5 ppm/K, more preferably at most 4.25 ppm/K, more preferably at most 4.0 ppm/K, more preferably at most 3.75 ppm/K, more preferably at most 3.5 ppm/K. In some embodiments, the

CTE is at least 2.50 ppm/K, at least 2.75 ppm/K, at least 3.00 ppm/K, at least 3.25 ppm/K, or at least 3.50 ppm/K. This refers to the value CTE, which can be calculated using formula (2) for glasses of this invention.

In order to identify an optimum trade-off between the above three properties, a highly precise selection of the working point is required.

Viscosity curve, especially working point (WP)

Surprisingly, a mixing rule can also be given for viscosity of glass, with which the viscosity is calculated from the viscosities of the constituent phases.

The starting point is the Adam-Gibbs relationship in its formulation for viscosity (see C.A. Angell, Structural Instability and Relaxation in Liquid and Glassy Phases near the fragile liquid limit, Journal of Non-Crystalline Solids 102 (1988) 205-221):

$$\eta = \eta_0 \cdot 10^{\frac{Q}{TS_c(T)}} \quad (3)$$

η_0 is a prefactor. Q is a constant. $S_c(T)$ is the configurational entropy, which according to Hodge is calculated from the configurational fraction $\Delta C_p(T)$ of the specific heat ("excess specific heat") under the assumption $\Delta C_p(T) = D/T$ by (see C.A. Angell, loc. cit., and the literature cited there):

$$S_c(T) = \int_{T_K}^T \frac{\Delta C_p}{T'} dT' = \frac{D}{T_K} - \frac{D}{T} \quad (4)$$

T_K is the Kauzmann temperature, which according to C.A. Angell, loc. cit., is identified with the Vogel-Fulcher-Tammann temperature T_0 . Thus, the Adam-Gibbs relation can be transformed into the Vogel-Fulcher-Tamman equation (VFT equation):

$$\eta = \eta_0 \cdot 10^{\frac{Q}{TS_c(T)}} = \eta_0 \cdot 10^{\frac{Q}{T \cdot D \cdot \left(\frac{1}{T_0} - \frac{1}{T}\right)}} = \eta_0 \cdot 10^{\frac{Q \cdot T_0}{D \cdot (T - T_0)}} =: 10^{A + \frac{B}{T - T_0}} \quad (5)$$

A , B , T_0 are the parameters of the VFT equation, which are determined by fit to a measurement curve.

With the assumptions of Angell and Hodge, Adam-Gibbs and VFT correspond to each other. Thus, the parameters η_0 and D/Q , which are in the Adam-Gibbs relationship, can be calculated from the VFT parameters A , B , T_0 .

$$\eta_0 = 10^A \text{ dPa} \cdot \text{s} \quad (6a)$$

$$\frac{D}{Q} = \frac{T_0}{B} \quad (6b)$$

From the relationships between Adam-Gibbs and VFT, a mixing rule can be derived that can be used to calculate the VFT parameters of a glass from the VFT parameters of the constituent phases known from measurements.

The first approach is:

$$\eta = \eta_0 \cdot 10^{\frac{Q}{TS_c(T)}} \text{ mit } S_c(T) = \text{const.} \cdot \left(\frac{1}{T_0} - \frac{1}{T} \right) = \sum_i v_i \cdot \text{const.}_i \cdot \left(\frac{1}{T_{0,i}} - \frac{1}{T} \right) \quad (7)$$

It is used here that the entropy is an additive quantity and is summed over all constituent phases. The mixture entropy is neglected according to Conradt, loc. cit.

v_i is the fraction of the i -th constituent phase in atom% rather than in mol%; the fact that atom% have to be used here follows from the derivation of the Adam-Gibbs equation.

If in addition, one assumes that Q has one and the same value for all constituent phases as well as the glass formed by mixing them, one can calculate:

$$\frac{D}{Q} = \sum_i v_i \cdot \frac{D_i}{Q} \quad (8a)$$

$$T_0 = \frac{D}{Q} / \sum_i v_i \cdot \frac{D_i}{Q \cdot T_{0,i}} = \frac{D}{Q} / \sum_i v_i \cdot \frac{1}{B_i} \quad (8b)$$

$$B = \frac{Q \cdot T_0}{D} \quad (8c)$$

The values for D_i or D_i/Q refer to the individual constituent phases and are obtained from their VFT parameters A_i , B_i , $T_{0,i}$ according to (6). The sum over "i" is from 1 to n , as above.

With B and T_0 , two of the three VFT parameters of the glass formed by mixing the constituent phases are known.

For the determination of A , it is made use of that the VFT equation approaches an Arrhenius relationship $\eta = 10^{A+B/T}$ at high temperatures, and there are several literature references to an approximately linear relationship between A and B for an Arrhenius-conforming viscosity. This leads to the formula:

$$A = \left(\sum_i v_i \cdot \frac{A_i}{B_i} \right) \cdot B \quad (9)$$

" v_i " again refers to atomic percentages. The sum over "i" is from 1 to n , as above.

For the calculation of the VFT parameters of a glass expressed as a mixture of the constituent phases forming the basic system of the invention, the VFT parameters of these phases are required. These are:

Table 4

Constituent Phase	A	B/K	$T_0/^\circ\text{C}$
Lithium-Disilicate	0.29	2379.5	267.1
Spodumene	-3.5	7403	244.5
Albite	-5.3423	14847.05	-22.43
Orthoklas	-6.67035	19291.519	-96.0872
Disodiumzincosilicate	-1.752	3370.6	299.9
Cordierite	-4.50166	6790.97	418.162

Constituent Phase	A	B/K	T ₀ /°C
Silicon Dioxide	-6.01651	26018.9	-240.131
Diboron Trioxide	-0.0871546	1650.04	149.859
Magnesiummetaphosphate	-1.26	2197	391

The VFT parameters of Silica were obtained by adaptation to publically available measurement data. VFT parameters can be determined applying known measuring methods.

If A, B, T₀ are known from the formulas (8) - (9), the working point WP is calculated by transforming (5) according to:

$$WP = \frac{B}{4-A} + T_0 \quad (10)$$

and the annealing point AP according to:

$$AP = \frac{B}{13-A} + T_0 \quad (11)$$

For example, mixing the constituent phases SiO₂ and B₂O₃ in a molar ratio of 9 : 1 or 0.9 : 0.1 which is equivalent to an atomic ratio of 9*3/(9*3+1*5) : 1*5/(9*3+1*5) (note that SiO₂ has 3 atoms whereas B₂O₃ has 5 atoms), we first obtain according to equation (25b) D_{SiO₂}/Q = (273.2-240.131)/26018.9 = 0.00127 and D_{B₂O₃}/Q = (273.2+149.859)/1650.5 = 0.25632. From this, the mixture is calculated according to equation (27a) D/Q = (9*3*D_{SiO₂}/Q + 1*5*D_{B₂O₃}/Q)/(9*3+1*5) = 0.04112. From this, the T₀ value of the mixture is calculated according to equation (27b) T₀ = 0.04112/((9*3/26018.9+1*5/1650.5)/(9*3+1*5)) = 323.533 K, i.e. 50.333°C. According to equation (27c), the B value of the mixture is calculated as 323.533K/0.04112 = 7868.03K. According to equation (28), A = (9*3*(-6.01651)/26018.9+1*5*(-

$0.0871546/1650.04)/((9*3+1*5)/7868.03) = -1.6$. This gives the working point WP as $(7868.03/5.6+323.533)$ K = 1728.54 K, i.e. 1455.34 °C, and the annealing point AP to $(7868.03/5.6+323.533)$ K = 862.439 K, i.e. 589.239 °C.

With respect to flat glass production, e.g., by drawing, the working point is advantageously at most 1400°C, more advantageously at most 1390°C, more advantageously at most 1380°C, more advantageously at most 1370°C, more advantageously at most 1360°C, more advantageously at most 1350°C, more advantageously at most 1340°C, more advantageously at most 1330°C, more advantageously at most 1320°C, more advantageously at most 1310°C, more advantageously at most 1300°C, more advantageously at most 1290°C, more advantageously at most 1280°C, more advantageously at most 1270°C, more advantageously at most 1260°C, more advantageously at most 1250°C.

Selection of constituent phases

The selection of the constituent phases according to this invention has been performed with respect to their suitability for usp-laser-structuring, expansion coefficient, working point, devitrification and mechanical properties. By “working point”, the temperature is addressed where the viscosity value is 10^4 dP·s, a typical viscosity for the melting and hot forming range. In the following, the role of the individual constituent phases in this invention is discussed in detail.

Lithium-Disilicate

Glassy Lithium Disilicate addresses the core of the invention disclosed by US 7262144 B2 from 2007 (“A preferred LAS glass [...] has a composition of from 15 to 90% by weight of SiO₂, from 1 to 35% by weight of Al₂O₃, and from 1 to 20% by weight of Li₂O.”), i.e., a LAS system with preferably a higher molar fraction of Li₂O than of Al₂O₃. So the two essential constituent phases needed to capture the basic idea of US 7262144 B2 are a Lithium-Silicate (for this invention, Lithium-Disilicate has been selected) and a Lithium-Aluminium-Silicate (for this invention, Spodume has been selected).

One mole of Lithium-Disilicate is understood to be one mole of $(\text{Li}_2\text{O} \cdot 2\text{SiO}_2)/3$.

The total Lithium fraction as provided by the two above constituent phases preferably exceeds 4mol%, more preferred 6mol%, more preferred 8mol%, more preferred 10mol%, more preferred 12mol%, more preferred 14mol%, more preferred 16mol%, more preferred 18mol%, more preferred 20mol%, more preferred 22mol%, more preferred 24mol%, more preferred 26mol%, more preferred 28mol%, more preferred 30mol%, more preferred 32mol%.

Spodumen

Glassy Spodumene is the other essential constituent phase which addresses the core of the invention disclosed by US 7262144 B2 from 2007. It contains both Lithium (see above) and Aluminium. As the latter is only slightly lighter than Silicon, it is not assumed to significantly contribute to the essential effect of refractive index increase in the centre of the usp-laser focus.

One mole of Spodumene is understood to be one mole of $(\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2)/6$.

Albite

Glassy Albite is added one of the constituent phases according to the invention to provide an additional degree of freedom concerning the adjustment of the thermal expansion and the working point. As Sodium is only slightly lighter than Silicon, Albite is assumed to contribute less to the essential effect of refractive index increase in the centre of the usp-laser focus than the Lithium-containing phases.

One mole of Albite is understood to be one mole of $(\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2)/8$.

Orthoklas

Glassy Orthoklas is the potassium analogon of albite and another constituent phase according to the invention. As glass compositions which include both sodium and at least a small fraction of potassium are less sensitive to devitrification, a small amount of Orthoklas may be added to the composition. In terms of atom weight,

however, a Potassium-containing phase is disadvantageous with respect to the essential effect of US 7262144 B2 from 2007.

One mole of Orthoklas is understood to be one mole of $(K_2O \cdot Al_2O_3 \cdot 6SiO_2)/8$.

Disodium-Zinco-Silicate

Glassy Disodium-Zinco-Silicate is added to the constituent phases according to the invention to provide an additional degree of freedom with respect to adjusting thermal expansion and working point. In terms of atom weight, however, a Zinc-containing phase is disadvantageous with respect to the essential effect of US 7262144 B2 from 2007.

One mole of Disodium-Zinco-Silicate is understood to be one mole of $(Na_2O \cdot ZnO \cdot 3SiO_2)/5$.

Cordierite

Glassy Cordierite is added as one of the constituent phases according to the invention to provide an additional degree of freedom concerning the adjustment of the thermal expansion and the working point. As Magnesium is only slightly lighter than Silicon, Cordierite is assumed to contribute less to the essential effect of refractive index increase in the centre of the usp-laser focus than the Lithium-containing phases.

One mole of Cordierite is understood to mean one mole of $(2MgO \cdot 2Al_2O_3 \cdot 5SiO_2)/9$.

SiO₂

To begin with, glassy SiO₂ is essential to push down the coefficient of expansion and thus, on balance, to desired values.

B₂O₃

To begin with, glassy B₂O₃ is also suitable to push down the coefficient of expansion and thus, on balance, to desired values.

Diboron trioxide forms boroxol rings as a constituent phase, which have a favourable effect on the mechanical properties.

There is another reason to introduce diboron trioxide as a constituent phase in the glass. This shifts the boron/sodium ratio to higher values, which lowers sodium and boron evaporation during melting and hot forming.

In view of the above-mentioned hygroscopy alone, diboron trioxide is unsuitable as a basic system for the glasses according to the invention, it is suitable only as an admixture.

With respect to its atomic weight, Boron may be expected to accumulate in the centre of the usp-laser-focus. With respect to its ultra-low polarizability, this is disadvantageous with respect to the essential effect of US 7262144 B2 from 2007.

Magnesiummetaphosphate

Glassy Magnesiummetaphosphate is added as one of the constituent phases according to the invention to provide an additional degree of freedom concerning the adjustment of the thermal expansion and the working point. As Magnesium is only slightly lighter than Silicon, Magnesiummetaphosphate is assumed to contribute less to the essential effect of refractive index increase in the centre of the usp-laser focus than the Lithium-containing phases. As Phosphorous is slightly heavier than Silicon, it may be expected to accumulate in the outside section of the usp-laser-focus. With respect to its ultra-low polarizability, this will not be disadvantageous with respect to the essential effect of US 7262144 B2.

One mole of Magnesiummetaphosphate is understood to mean one mole of $(\text{MgO} \cdot \text{P}_2\text{O}_5)/2$.

Further components

In addition to the components already mentioned, the glass may contain further constituents, referred to herein as "balance". The proportion of balance in the glass

according to the invention is preferably at most 5 mol-%, so as not to disturb the glass properties set by careful selection of suitable base glasses. In particularly preferred embodiments, the proportion of balance in the glass is at most 3 mol%, more preferably at most 2 mol% or at most 1 mol% or at most 0.5 mol%. The balance contains in particular oxides which are not contained in the base glasses mentioned herein. Thus, the balance in particular does not contain SiO_2 , B_2O_3 , Al_2O_3 , ZnO , MgO , Li_2O , Na_2O or K_2O . According to the invention, additions of further simple oxides of so-called "intermediates", i.e. oxides which stand between the network formers such as SiO_2 and the network converters such as Na_2O , are optionally used as the balance. Although these oxides do not form glasses on their own, they can be incorporated into the network in the aforementioned percentage range. Thus, the balance may contain, in particular, oxides such as TiO_2 . Ta_2O_5 also belongs to the "intermediates", as can be seen using the ionic radii.

When this description states that the glasses are free of a component or constituent phase or do not contain a certain component or constituent phase, it is meant that this component or constituent phase may be present at most as an impurity in the glasses. This means that it is not added in substantial amounts. According to the invention, non-substantial amounts are amounts of less than 500 ppm (molar), preferably less than 300 ppm (molar), particularly preferably less than 100 ppm (molar), even more preferably less than 50 ppm (molar), and most preferably less than 10 ppm (molar). Preferably, the glasses of the present invention are free of lead, arsenic, antimony, and/or cadmium.

Other Glass Properties

The glass according to this invention will preferably be provided as sheet or endless sheet, with a medium thickness of $30\mu\text{m}$ to 3mm.

Production

Also, according to the invention is a method for producing a glass of the present invention, comprising the steps of:

- Melting the glass raw materials,
- optionally forming a glass article, in particular a glass sheet, from the molten glass
- Cooling of the glass.

Forming the glass may comprise a drawing process or a floating process. Cooling may involve active cooling using a coolant, such as a cooling fluid, or passive cooling.

Uses and glass articles

According to the invention, the glass may be used as substrate glass in an electronic and/or optoelectronic device. It is especially suitable to inscribe waveguides by usp-laser inscription into the glass substrate and/or to mount semiconductor elements on it, including the coupling to semiconductor devices and/or substrates.

For example, a corresponding glass has a thermal expansion coefficient CTE that is at most 8 ppm/K or which ranges especially from 2.5 ppm/K to 8 ppm/K and wherein preferably the working point is at most 1400°C.

Another beneficial embodiment foresees that the Lithium fraction is at least 4.0 mol%. Especially, the Lithium fraction is calculated by a matrix represented by aforesaid table 7 of this description.

The invention also covers a substrate comprising the glass described above, wherein the glass contains an inscribed waveguide and/or wherein the substrate is mounted to a semiconductor device, or the semiconductor device is mounted to a substrate areas comprising the aforesaid glass.

The invention relates to an electronic or optoelectronic device as well which comprises the glass or the substrate described above.

Advantageously, the electronic or optoelectronic device according to the invention comprises a semiconductor device or substrate which has a CTE from 2.6 to 3.4 ppm/K and preferably the glass has a CTE from 2.5 to 3.6 ppm/K.

The method of inscribing a waveguide into a substrate, comprising the steps of providing a usp-laser source and directing a focused laser beam from said usp-laser source onto the substrate, whereas the substrate is selected from a glass described above, is also subject to the invention.

Suitable lasers for waveguide inscription are ultra short pulse lasers, thus lasers that emit their power as pulse trains, where the temporal distance between the pulses is $1/R$, with R being the repetition rate of the laser. The repetition rate can be in the range from 1 Hz to 100 GHz, but preferred, 1 kHz, 10 kHz, 50 kHz, 100 kHz, 500 kHz, 1 MHz. The pulse duration (FWHM, full width, half max) of these lasers is typically between 30 fs up to 20 ps. For waveguide inscription the preferred duration is 80 fs to 300 fs, most preferred 100 fs. They emit their laser light at center wavelength of 800 nm in case of Titanium-Sapphire lasers or at 1030 nm or 1064 nm for Nd:YAG lasers. However, for some wave guide inscription processes, converting the laser wavelength into the VIS range can be favourable, e.g. with second harmonic generation (SHG) or third harmonic generation (THG) by means of non-linear crystals. Thus, the center wavelengths can also be 200 nm, 355 nm, 400 nm, 515 nm, 532 nm, The spectral bandwidth can be 1 nm and up to 100 nm. The output beam parameter of the collimated laser beam is usually 3 to 5 mm ($1/e^2$), but can also be increased with telescope setup to 10 mm or 20 mm. Some of these lasers can not only emit their energy single pulses, but also divide the energy in sub-pulse trains, so-called "burst", where the inter-subpulse distance Δt_p is much smaller than $1/R$, typically in the range of 1-200 ns, most preferred to be 20 ns – 30 ns. These burst consist of 2 to 50 sub pulses. Preferred are bursts of 2 to 4 or 3 to 7 sub pulses. The output power P of the lasers is typically between 1 W and 500 W. The pulse energy or burst energy is P/R . For the waveguide process pulse energies or burst energies of 0.1 to 8 μ J, preferred 0.5 to 2 μ J. For this regime it might be necessary to attenuate the output power of the laser system.

For the waveguide inscription microscope objectives or especially laser inscription objectives are used. While the microscope objectives are usually optimized for imaging in the VIS range, laser inscription objectives are designed to focus a collimated, quasi-monochromatic laser beam to a diffraction limited spot. In both cases, the objective can be characterized by its numerical aperture (NA), the ratio of the half opening aperture to the nominal focal length. For waveguide inscription, NA of 0.05 to 0.8 are suitable, the preferred NA is 0.1, 0.2 or 0.4. For the waveguide inscription, the laser beam is incident on the input aperture of the objective and the glass substrate is placed, so that the focal point of the objective is located within the glass substrate.

The translation velocity is the velocity the focus of the objective is moved relative to the glass substrate. This can be achieved by translating the sample via a motion controlled stage or by moving the laser focus, e.g. with a mirror ensemble that ensures that the laser beam is still incident on the input aperture of the objective, when the objective is moved with a mechanical axis. Another implementation is the integration of deformable mirror or a spatial light modulator (SLM) before the objective; thus translating the spot by imprinting a defocus and/or a tilt on the wavefront of the incident beam. Also a combination of both of the translation mechanisms can be favorable, e.g. for achieving precision for longer modification lines. The translation velocities are in the range of 1 mm/s to 10 m/s, preferably 10 mm/s to 1 m/s, most preferred 20 mm/s to 200 mm/s, mostly preferred 50 mm/s to 100 mm/s. It can also be favorable to set the translation velocity v in relation to the repetition rate of the laser R in order to achieve a periodicity of $\Lambda = v/R$. For waveguides with a double function as Bragg-Reflectors Λ is in the range of 100 nm to 10 μm , most preferred 200 nm to 2 μm , mostly preferred 500 nm to 1.5 μm . For steering the inherent waveguide properties, much smaller periodicities Λ of 0.1 to 10 nm are favourable, most preferred 0.2 to 5 nm. A combination of two modifications can be achieved with pulse bursts: the longer periodicity is steered with the repetition rate R to be $\Lambda_{\text{large}} = v/R$, while the smaller periodicity is steered with inter-subpulse distance Δt_p to be $\Lambda_{\text{small}} = v \cdot \Delta t_p$.

With these laser parameters a local raise of the refractive index of $\Delta n_{\max}$ of up to 0.005 can be achieved with in the modification line. The preferred Δn is in the range of 0.0001 to 0.002, mostly preferred 0.0005 to 0.005. By adjusting certain laser parameters, e.g. the pulse energy, the Δn can be continuously altered. This can be done during inscription, so that Δn varies along the modification line of length L . The variation of can be linear or non-linear function of the modification line coordinate l , $0 < l < L$. It can also be periodic or an-periodic.

For the waveguiding properties, the transversal refractive index profile of the modification line is relevant. For the following, we introduce the local coordinate vectors x and y , which are both perpendicular to the modification line vector z and centered at the modification line. For most laser parameters, the refractive index profile $\Delta n(x,y)$ is approximately rectangular: e.g. it can be described with $\Delta n(x,y) = \Delta n_{\max}$ for $|x| < w_x/2$ and $|y| < w_y/2$ and $\Delta n = 0$ elsewhere. Here w_x and w_y are the transversal widths of the waveguides, which are typically 0.2 μm to 100 μm , most preferred 0.5 to 20 μm , mostly preferred 1-15 μm , more mostly preferred 2-12 μm .

However, due to the Soret effect, for the glass substrates in this invention, the refractive crosssection of the waveguide can be steered with the aforementioned laser parameters, so that the profile is more gradient like, e.g. $\Delta n(x,y) = \Delta n_{\max} - (a_1|x| + a_2x^2 + a_3|x|^3 + a_4x^4 + \dots + b_1|y| + b_2y^2 + b_3|y|^3 + b_4y^4 + \dots)$. This profile can also be altered along the modification line. In this case we relate to the FWHM definition of the waveguide width along the local x and y axis.

The waveguides lines of this invention have low losses for light at the wavelength of 1550 nm, namely below 1 dB/cm, preferably 0.5 dB/cm, most preferred smaller than 0.3 dB/cm, mostly preferred below 0.1 dB/cm.

Also provided herein is a method of manufacturing an electronic or optoelectronic device, comprising the steps of mounting a semiconductor element to an element comprising the glass according to this description.

Advantageously, the invention is represented in a method of manufacturing an electronic or optoelectronic device comprising a semiconductor element and a glass substrate, comprising the steps of determining the CTE of the semiconductor element, then selecting the CTE of glass of the glass substrate by selecting a composition range of the glass according to this description.

Examples

For comparison with the prior art, we first provide a conversion matrix for the mutual conversion of both compositional data.

The composition in constituent phases is given in the following normalized form for the purpose of conversion:

Table 5

Constituent phase	Normalized formula
Lithium-Disilicate	$(\text{Li}_2\text{O} \cdot 2\text{SiO}_2)/3$
Spodumene	$(\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2)/6$
Albite	$(\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2)/8$
Orthoklas	$(\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2)/8$
Disodium-Zinco-Silicate	$(\text{Na}_2\text{O} \cdot \text{ZnO} \cdot 3\text{SiO}_2)/5$
Cordierite	$(2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2)/9$
Silicon Dioxide	SiO_2
Diboron-Trioxide	B_2O_3
Magnesiummetasilicate	$(\text{MgO} \cdot \text{P}_2\text{O}_5)/2$

The conversion of these compositions into a composition statement in mol% with respect to the following simple oxides ...

Table 6

#	Oxid
1.	SiO ₂
2.	B ₂ O ₃
3.	Al ₂ O ₃
4.	ZnO
5.	MgO
6.	Li ₂ O
7.	Na ₂ O
8.	K ₂ O
9.	P ₂ O ₅

... is carried out with the aid of the matrix given here. The composition in mol% with respect to the constituent phases is multiplied as a column vector from the right to the matrix:

Table 7: Matrix

$$\begin{pmatrix} \frac{2}{3} & \frac{4}{6} & \frac{6}{8} & \frac{6}{8} & \frac{3}{5} & \frac{5}{9} & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & \frac{1}{6} & \frac{1}{8} & \frac{1}{8} & 0 & \frac{2}{9} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{5} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{2}{9} & 0 & 0 & \frac{1}{2} \\ \frac{1}{3} & \frac{1}{6} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{8} & 0 & \frac{1}{5} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{8} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} \end{pmatrix} \times \begin{pmatrix} (Li_2O \cdot 2SiO_2)/3 \\ (Li_2O \cdot Al_2O_3 \cdot 4SiO_2)/6 \\ (Na_2O \cdot Al_2O_3 \cdot 6SiO_2)/8 \\ (K_2O \cdot Al_2O_3 \cdot 6SiO_2)/8 \\ (Na_2O \cdot ZnO \cdot 3SiO_2)/5 \\ (2MgO \cdot 2Al_2O_3 \cdot 5SiO_2)/9 \\ SiO_2 \\ B_2O_3 \\ (MgO \cdot P_2O_5)/2 \end{pmatrix} \quad (12)$$

As a result of the multiplication of the column vector to the matrix, the composition of the glass in mole percent with respect to simple oxides is obtained.

As a result of the multiplication of the column vector to the inverse matrix, the composition of the glass in mole percent with respect to constituent phases is obtained.

As reference, we consider a composition that comes close to example #8 of US7262144B2 by Schreder et al.

Table 8a: Reference in constituent phases

Constituent phase	Normalized formula	Fraction / mol%
Lithium-Disilicate	$(Li_2O \cdot 2SiO_2)/3$	52.53
Spodumene	$(Li_2O \cdot Al_2O_3 \cdot 4SiO_2)/6$	0
Albite	$(Na_2O \cdot Al_2O_3 \cdot 6SiO_2)/8$	0
Orthoklas	$(K_2O \cdot Al_2O_3 \cdot 6SiO_2)/8$	17.84

Constituent phase	Normalized formula	Fraction / mol%
Disodium-Zinco-Silicate	$(\text{Na}_2\text{O} \cdot \text{ZnO} \cdot 3\text{SiO}_2)/5$	3.4
Cordierite	$(2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2)/9$	0
Silicon Dioxide	SiO_2	26.22
Diboron-Trioxide	B_2O_3	0
Magnesiummetasilicate	$(\text{MgO} \cdot \text{P}_2\text{O}_5)/2$	0

Table 9b: Reference in simple oxides

Oxide	Fraction / mol%
SiO_2	76.66
B_2O_3	0
Al_2O_3	2.23
ZnO	0.68
MgO	0
Li_2O	17.51
Na_2O	0.68
K_2O	2.23
P_2O_5	0

The calculated properties are:

1. The thermal expansion coefficient calculated according to (2) amounts to 9.45 ppm/K.
2. The working point calculated according to (10) amounts to 1169.99°C.

The first example is a glass with the composition:

Table 9a: Example 1 in constituent phases

Constituent phase	Normalized formula	Fraction / mol%
Lithium-Disilicate	$(\text{Li}_2\text{O} \cdot 2\text{SiO}_2)/3$	20
Spodumene	$(\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2)/6$	20
Albite	$(\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2)/8$	5
Orthoklas	$(\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2)/8$	5
Disodium-Zinco-Silicate	$(\text{Na}_2\text{O} \cdot \text{ZnO} \cdot 3\text{SiO}_2)/5$	0
Cordierite	$(2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2)/9$	0
Silicon Dioxide	SiO_2	44
Diboron-Trioxide	B_2O_3	0
Magnesiummetasilicate	$(\text{MgO} \cdot \text{P}_2\text{O}_5)/2$	6

Table 10b: Example 1 in simple oxides

Oxide	Fraction / mol%
SiO ₂	78.1667
B ₂ O ₃	0
Al ₂ O ₃	4.58333,
ZnO	0
MgO	3
Li ₂ O	10
Na ₂ O	0.625
K ₂ O	0.625
P ₂ O ₅	3

The calculated properties are:

1. The thermal expansion coefficient calculated according to (2) amounts to 5.91 ppm/K.
2. The working point calculated according to (10) amounts to 1294°C.

The next example is a glass with the composition:

Table 10a: Example 2 in constituent phases

Constituent phase	Normalized formula	Fraction / mol%
Lithium-Disilicate	$(\text{Li}_2\text{O} \cdot 2\text{SiO}_2)/3$	20
Spodumene	$(\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2)/6$	25
Albite	$(\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2)/8$	5
Orthoklas	$(\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2)/8$	0
Disodium-Zinco-Silicate	$(\text{Na}_2\text{O} \cdot \text{ZnO} \cdot 3\text{SiO}_2)/5$	0
Cordierite	$(2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2)/9$	0
Silicon Dioxide	SiO_2	44
Diboron-Trioxide	B_2O_3	0
Magnesiummetasilicate	$(\text{MgO} \cdot \text{P}_2\text{O}_5)/2$	6

Table 11b: Example 2 in simple oxides

Oxide	Fraction / mol%
SiO_2	77.75
B_2O_3	0
Al_2O_3	4.79167
ZnO	0
MgO	3

Oxide	Fraction / mol%
Li ₂ O	10.8333
Na ₂ O	0.625
K ₂ O	0
P ₂ O ₅	3

The calculated properties are:

1. The thermal expansion coefficient calculated according to (2) amounts to 5.96 ppm/K.
2. The working point calculated according to (10) amounts to 1273°C.

The next example is a glass with the composition:

Table 11a: Example 3 in constituent phases

Constituent phase	Normalized formula	Fraction / mol%
Lithium-Disilicate	(Li ₂ O·2SiO ₂)/3	25
Spodumene	(Li ₂ O·Al ₂ O ₃ ·4SiO ₂)/6	25
Albite	(Na ₂ O·Al ₂ O ₃ ·6SiO ₂)/8	5
Orthoklas	(K ₂ O·Al ₂ O ₃ ·6SiO ₂)/8	0
Disodium-Zinco-Silicate	(Na ₂ O·ZnO·3SiO ₂)/5	0
Cordierite	(2MgO·2Al ₂ O ₃ ·5SiO ₂)/9	0
Silicon Dioxide	SiO ₂	39

Constituent phase	Normalized formula	Fraction / mol%
Diboron-Trioxide	B ₂ O ₃	0
Magnesiummetasilicate	(MgO·P ₂ O ₅)/2	6

Table 12b: Example 3 in simple oxides

Oxide	Fraction / mol%
SiO ₂	76.0833
B ₂ O ₃	0
Al ₂ O ₃	4.79167
ZnO	0
MgO	3
Li ₂ O	12.5
Na ₂ O	0.625
K ₂ O	0
P ₂ O ₅	3

The calculated properties are:

1. The thermal expansion coefficient calculated according to (2) amounts to 6.63 ppm/K.
2. The working point calculated according to (10) amounts to 1224°C.

The next example is a glass with the composition:

Table 12a: Example 4 in constituent phases

Constituent phase	Normalized formula	Fraction / mol%
Lithium-Disilicate	$(\text{Li}_2\text{O} \cdot 2\text{SiO}_2)/3$	35
Spodumene	$(\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2)/6$	15
Albite	$(\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2)/8$	0
Orthoklas	$(\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2)/8$	0
Disodium-Zinco-Silicate	$(\text{Na}_2\text{O} \cdot \text{ZnO} \cdot 3\text{SiO}_2)/5$	0
Cordierite	$(2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2)/9$	0
Silicon Dioxide	SiO_2	46
Diboron-Trioxide	B_2O_3	1
Magnesiummetasilicate	$(\text{MgO} \cdot \text{P}_2\text{O}_5)/2$	3

Table 13b: Example 4 in simple oxides

Oxide	Fraction / mol%
SiO_2	79.3333
B_2O_3	1
Al_2O_3	2.5

Oxide	Fraction / mol%
ZnO	0
MgO	1.5
Li ₂ O	14.1667
Na ₂ O	0
K ₂ O	0
P ₂ O ₅	1.5

The calculated properties are:

1. The thermal expansion coefficient calculated according to (2) amounts to 6.7 ppm/K.
2. The working point calculated according to (10) amounts to 1237°C.

The next example is a glass with the composition:

Table 13a: Example 5 in constituent phases

Constituent phase	Normalized formula	Fraction / mol%
Lithium-Disilicate	(Li ₂ O·2SiO ₂)/3	20
Spodumene	(Li ₂ O·Al ₂ O ₃ ·4SiO ₂)/6	45
Albite	(Na ₂ O·Al ₂ O ₃ ·6SiO ₂)/8	0
Orthoklas	(K ₂ O·Al ₂ O ₃ ·6SiO ₂)/8	0
Disodium-Zinco-Silicate	(Na ₂ O·ZnO·3SiO ₂)/5	0

Constituent phase	Normalized formula	Fraction / mol%
Cordierite	$(2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2)/9$	5
Silicon Dioxide	SiO_2	30
Diboron-Trioxide	B_2O_3	0
Magnesiummetasilicate	$(\text{MgO} \cdot \text{P}_2\text{O}_5)/2$	0

Table 14b: Example 5 in simple oxides

Oxide	Fraction / mol%
SiO_2	76.1111
B_2O_3	0
Al_2O_3	8.61111
ZnO	0
MgO	1.11111
Li_2O	14.1667
Na_2O	0
K_2O	0
P_2O_5	0

The calculated properties are:

1. The thermal expansion coefficient calculated according to (2) amounts to 6.92 ppm/K.

2. The working point calculated according to (10) amounts to 1283°C.

The next example is a glass with the composition:

Table 14a: Example 6 in constituent phases

Constituent phase	Normalized formula	Fraction / mol%
Lithium-Disilicate	$(\text{Li}_2\text{O} \cdot 2\text{SiO}_2)/3$	30
Spodumene	$(\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2)/6$	40
Albite	$(\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2)/8$	0
Orthoklas	$(\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2)/8$	0
Disodium-Zinco-Silicate	$(\text{Na}_2\text{O} \cdot \text{ZnO} \cdot 3\text{SiO}_2)/5$	0
Cordierite	$(2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2)/9$	5
Silicon Dioxide	SiO_2	25
Diboron-Trioxide	B_2O_3	0
Magnesiummetasilicate	$(\text{MgO} \cdot \text{P}_2\text{O}_5)/2$	0

Table 15b: Example 6 in simple oxides

Oxide	Fraction / mol%
SiO_2	74.4444
B_2O_3	0
Al_2O_3	7.77778
ZnO	0

Oxide	Fraction / mol%
MgO	1.11111
Li ₂ O	16.6667
Na ₂ O	0
K ₂ O	0
P ₂ O ₅	0

The calculated properties are:

3. The thermal expansion coefficient calculated according to (2) amounts to 7.9 ppm/K.
4. The working point calculated according to (10) amounts to 1211°C.

The next example is a glass with the composition:

Table 15a: Example 7 in constituent phases

Constituent phase	Normalized formula	Fraction / mol%
Lithium-Disilicate	(Li ₂ O·2SiO ₂)/3	24
Spodumene	(Li ₂ O·Al ₂ O ₃ ·4SiO ₂)/6	3
Albite	(Na ₂ O·Al ₂ O ₃ ·6SiO ₂)/8	0
Orthoklas	(K ₂ O·Al ₂ O ₃ ·6SiO ₂)/8	0
Disodium-Zinco-Silicate	(Na ₂ O·ZnO·3SiO ₂)/5	0

Constituent phase	Normalized formula	Fraction / mol%
Cordierite	$(2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2)/9$	0
Silicon Dioxide	SiO_2	65
Diboron-Trioxide	B_2O_3	0
Magnesiummetasilicate	$(\text{MgO} \cdot \text{P}_2\text{O}_5)/2$	8

Table 16b: Example 7 in simple oxides

Oxide	Fraction / mol%
SiO_2	83
B_2O_3	0
Al_2O_3	0.5
ZnO	0
MgO	4
Li_2O	8.5
Na_2O	0
K_2O	0
P_2O_5	4

The calculated properties are:

1. The thermal expansion coefficient calculated according to (2) amounts to 4.63 ppm/K.
2. The working point calculated according to (10) amounts to 1323°C.

The invention described herein provides the advantage that it provides a glass which fulfills two requirements, first a waveguide can be inscribed which has a good performance, i.e. low damping, because of the high difference of refractive index of the waveguide and the substrate it is embedded in. Secondly, the glass described herein has a comparably low CTE, so it can be adapted or even matched to the CTE of semiconductor substrate materials, such as silicon. A further advantage is, that the glass can be rationally produced by industrial melting processes.

Patent Claims

1. Glass comprising the following constituent phases (in mol%):

Constituent Phase	min	max
Lithium-Disilicate	10	100
Spodumene	0	40
Albite	0	20
Orthoklas	0	20
Disodiumzincosilicate	0	20
Cordierite	0	20
Silicon Dioxide	0	50
Diboron Trioxide	0	5
Magnesiummetaphosphate	0	40

2. Glass according to claim 1, wherein the thermal expansion coefficient is at most 8ppm/K, especially from 2.5ppm/K to 8ppm/K, and wherein preferably the working point is at most 1400°C.
3. Glass according to at least one of the preceding claims, wherein the Lithium fraction is at least 4.0 mol%.
4. Glass according to claim 3, wherein the Lithium fraction is calculated by a matrix represented by table 7 of the description.

5. Substrate comprising the glass according to at least one of the preceding claims, wherein the glass contains an inscribed waveguide and/or wherein the substrate is mounted to a semiconductor device or substrate at least in an area comprising the glass.
6. Electronic or optoelectronic device comprising the glass or the substrate according to at least one of the preceding claims.
7. Electronic or optoelectronic device according to claim 6, wherein the semiconductor device or substrate has a CTE from 2.6 to 3.4 ppm/K and preferably the glass has a CTE from 2.5 to 3.6 ppm/K.
8. Method of inscribing a waveguide into a substrate, comprising the steps of providing a usp-laser source and directing a focused laser beam from said usp-laser source onto the substrate, whereas the substrate is selected from a glass according to at least one of the claims 1 to 4.
9. Method of manufacturing an electronic or optoelectronic device, comprising the steps of mounting a semiconductor element to an element comprising the glass according to at least one of the claims 1 to 4.
10. Method of manufacturing an electronic or optoelectronic device comprising a semiconductor element and a glass substrate, comprising the steps of determining the CTE of the semiconductor element, then selecting the CTE of glass of the glass substrate by selecting a composition range of the glass according to at least one of the claims 1 to 4.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/081193

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	C03C3/085	C03C3/097
	C03C23/00	G02B6/13
ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
C03C G02B		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2016/340228 A1 (SCHREDER BIANCA [DE] ET AL) 24 November 2016 (2016-11-24) paragraphs [0119], [0137], [0138]; claims; examples; tables -----	1 - 10
X	US 7 262 144 B2 (SCHOTT AG [DE]) 28 August 2007 (2007-08-28) cited in the application column 3, lines 4-9 column 12, lines 16-22; claims; examples; tables -----	1 - 10
X	EP 3 770 130 A1 (CDGM GLASS CO LTD [CN]) 27 January 2021 (2021-01-27) paragraph [0104]; claims; examples; tables -----	1 - 7, 9, 10
X	US 2017/210665 A1 (BEALL GEORGE HALSEY [US] ET AL) 27 July 2017 (2017-07-27) claims; figures; examples; tables -----	1 - 4
☐ Further documents are listed in the continuation of Box C.		
☒ See patent family annex.		
* Special categories of cited documents :		
"A" document defining the general state of the art which is not considered to be of particular relevance		"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date		"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"O" document referring to an oral disclosure, use, exhibition or other means		"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search		Date of mailing of the international search report
5 February 2025		19/02/2025
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Wrba, Jürgen

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