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(54) Title: ION-EXCHANGEABLE GLASSES WITH LOW Al₂O₃-CONTENT FOR DISPLAY DEVICES

(57) Abstract: This disclosure relates to glasses and glass articles made from glasses with low Al₂O₃-content. The glass articles include flat glass suitable for use in display devices, in particular foldable display devices, such as for electronic devices, including smartphones, smart watches and tablet computers. A method of making glass articles is described as well.



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Ion-exchangeable glasses with low Al_2O_3 -content for display devices

This disclosure relates to glasses and glass articles made from glasses with low Al_2O_3 -content. The glass articles include flat glass suitable for use in display devices, in particular foldable display devices, such as for electronic devices, including smartphones, smart watches and tablet computers. A method of making glass articles is described as well.

Background

Display devices, in particular foldable display devices, such as smartphones and tablet computers, are becoming more and more popular. Foldable devices combine the benefits of a large screen when unfolded and portable size when folded. In order for a glass sheet to be usable in such a foldable display device, it has to be extremely thin. A very thin glass is prone to breakage. Still, such a glass must be sufficiently strong to withstand repeated folding and unfolding operations.

Typically, aluminosilicate glasses were used in portable electronic devices. Aluminosilicate glass has certain properties that make it well suited for use as a display glass, especially in cases of display cover glasses which need to be flexible or foldable and have thicknesses below 100 μm . However, compressive stress diminishes in aluminosilicate glass with smaller thickness. Additionally, ways of further increasing the impact resistance in alkali aluminosilicates often lead to an increased tendency to devitrify during production which decreases yield. Consequently, a solution must be found to both increase the compressive stress even for thin glasses and maintain devitrification stability. Further, it would be advantageous if such new glasses would also possess an improved acid resistance since the glass surface of touch screens may be exposed to the acidic conditions of the user's skin.

It would be good to have a glass that overcomes the shortcomings of the prior art.

Summary of the disclosure

In a first aspect, this disclosure relates to a glass comprising the following components:

- i. SiO_2 ,
- ii. Al_2O_3 in an amount of 0.0 to 6.0% by weight,
- ii. ZrO_2 in an amount of at least 8.0% by weight,

- iii. Na₂O in an amount of at least 12.0% by weight,
- iv. 0.0 to 5.0% by weight of B₂O₃
- v. 0.0 to 5.0% by weight of Li₂O,
- vi. 0.0 to 10.0% by weight of K₂O; and
- vii. optionally, one or more components selected from P₂O₅ and TiO₂.

In a second aspect, this disclosure relates to a glass comprising the following components in percent by weight:

SiO ₂	40.0 to 70.0
Al ₂ O ₃	0.0 to 6.0
Na ₂ O	12.0 to 25.0
ZrO ₂	8.0 to 32.0
B ₂ O ₃	0.0 to 5.0
Li ₂ O	0.0 to 5.0
K ₂ O	0.0 to 10.0
MgO	0.0 to 20.0
CaO	0.0 to 15.0
MgO+CaO	at least 1.5
SrO	0.0 to 10.0
BaO	0.0 to 10.0
ZnO	0.0 to 10.0
P ₂ O ₅	0.0 to 10.0
TiO ₂	0.0 to 5.0
Y ₂ O ₃	0.0 to 20.0
La ₂ O ₃	0.0 to 10.0
Nb ₂ O ₅	0.0 to 10.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

and, optionally, comprising a dye or colorant such as Fe₂O₃, CoO, and/or Cr₂O₃.

The inventors found that the glass according to the first and second aspects provides for a novel combination of desirable properties. It was found that prior art glasses have insufficient

devitrification stability and impact resistance, even after chemical strengthening. Thus, to improve the impact resistance and maintaining devitrification stability, the glasses of this disclosure were developed.

In the present disclosure, an improved packing density was achieved by significantly reducing Al_2O_3 and significantly increasing the ZrO_2 content. Zirconium is octahedrally coordinated in the glass network, so that the packing density is higher than in the alkali aluminosilicates that are usually used. When Al_2O_3 is limited to $< 5 \text{ wt}\%$ a production with high yields (devitrification stability) is achieved. Further, due to the low working points (at least at those temperatures, at which the viscosity is equal to or less than $10^4 \text{ dPa}\cdot\text{s}$) of the alkali zirconium silicates compared to the commonly used aluminosilicates, such glasses may be produced at lower temperatures, so that both the environment is protected, and energy costs can be reduced.

Despite the rather low Al_2O_3 -content, the glass has surprisingly remarkable susceptibility to chemical strengthening. This means that when immersed in a salt bath for chemical toughening, the glass will build a high compressive stress on its surface within a very short time. In an embodiment, this compressive stress susceptibility will be as high as 800 MPa, or even 900 MPa or even 1000 MPa or even 1100 MPa or higher within 30 minutes of chemical toughening. Despite this remarkable susceptibility to compressive stress, the glass has only moderate thermal expansion, such as a coefficient of thermal expansion of less than 9.8 ppm/K or even less than 9.0 ppm/K. This very moderate thermal expansion allows for the production of articles with excellent dimensional characteristics. During production of thin glass, for example in a down draw process, the glass will experience fast cooling. Typically, the cooling rates will not be exactly the same for all portions of the glass. This will lead to warp in the glass article. Warp will be higher for articles made of glass with higher coefficients of thermal expansion. Because the glass of this disclosure has low coefficients of thermal expansion, glass articles with particularly low warp can be produced.

Further, the glass of this disclosure also has excellent chemical resistance, in particular acid resistance. Chemical resistance is very useful in glass for display applications. Prior art glasses with considerable chemical strengthening characteristics usually have mediocre or insufficient chemical resistance. In one embodiment, the acid resistance class of the glass may be class 2 or better, the alkali resistance class of the glass may be class 2 or better, and the hydrolytic resistance class of the glass may be at least class 4 or better.

In a third aspect, this disclosure relates to a glass article comprising or consisting of a glass described herein.

In a fourth aspect, this disclosure relates to a glass article having less than 1000 μm thickness, wherein the article comprises a glass comprising SiO_2 in an amount of at least 40.0% by weight, Na_2O in an amount of at least 12.0% by weight, further comprising ZrO_2 , wherein the ratio of the amount by weight of ZrO_2 to the sum of the amounts by weight of Al_2O_3 and B_2O_3 is at least 1.5, the glass having a $\text{CSS}_{30\mu\text{m}}$ of at least 700 MPa and/or having an acid resistance of less than 5.0 mg/dm^2 , or an acid resistance of less than 2.5 mg/dm^2 .

In a fifth aspect, this disclosure relates to a glass article comprising or consisting of a glass described herein and comprising an ion-exchanged layer on one or both of its major surfaces.

In a sixth aspect, this disclosure relates an electronic device comprising a glass or a glass article as described herein.

In a seventh aspect, this disclosure relates to a method of making a glass, or a glass article of this disclosure.

Detailed description

Definitions

Coefficient of thermal expansion („CTE“) is the average coefficient of linear thermal expansion in a temperature range from 20°C to 300°C. It is determined in accordance with DIN ISO 7991:1987.

Compressive stress susceptibility (“CSS”, or “CSS score”) is given in MPa. It is the amount of compressive stress measured in a specimen of the glass under specific test conditions. For this test, the specimen may be in the form of a sheet of 200 μm or 30 μm thickness. The specimen is subjected to ion exchange treatment in an alkali nitrate salt bath (100%) for a duration of 30 minutes, wherein for small glass thicknesses (< 35 μm) the duration of chemical toughening can be reduced, e.g., to 15 minutes. The temperature may be chosen such that the highest chemical stress is obtained. The alkali nitrate salt depends on the kind of ion exchange treatment to be performed, i.e., which ions need to be exchanged. Optionally, the alkali nitrate salt is KNO_3 and the bath temperature is 440°C. The fact that a specimen of 200 μm or 30 μm thickness in the form of a sheet is used to determine CSS does not mean a restriction to glass articles in sheet form, or even to sheets of that thickness. Instead, CSS is a property of the glass material that is measured on a sheet prepared from the glass. Whereas CSS is influenced by the thermal history of a glass, it is a feature of the glass material or glass articles. Notably, CSS is a feature of the un-strengthened material or article, i.e., untreated by ion exchange. The different

thicknesses that the CSS values relate to are indicated as an index, e.g., $CSS_{30\mu m}$ for a 30 μm thick sheet.

“1000 MPa IOX-time” is the time of ion exchange treatment needed by a glass to build a compressive stress on its surface of at least 1000 MPa. The corresponding experiment is the same as for CSS measurement, i.e., the specimen is a 200 μm thick glass sheet immersed in an alkali nitrate bath. The temperature may be chosen at 380°C for sodium nitrate baths, and at 440°C for the other alkali nitrates. The “1000 MPa IOX-time” is reached when the specimen has a compressive stress of at least 1000 MPa.

Compressive stress (CS) is the induced compression of the glass network after ion exchange on the surface layer of glass. CS usually decreases from a maximum value at the surface of the glass layer (surface CS) towards the inside of the glass layer. As is customary in the art, any indication of CS in this disclosure relates to the maximum value of the respective surface. Commercially available test machines such as FSM6000LE (company ORIHARA INDUSTRIAL CO. LTD) or SLP1000 (company “ORIHARA”, Japan) can be used to measure the CS.

Depth of layer (DoL) is the thickness of the layer at the surface of a glass article where CS exists, which essentially corresponds to the thickness of an ion exchanged layer. Commercially available test machines such as FSM6000 (company “Luceo Co., Ltd.”, Japan/Tokyo) can be used to measure the DoL by a wave guide mechanism.

“Diffusivity” (D in $\mu m^2/h$) is a material property of a glass that describes its ability to build an ion-exchanged layer upon chemical toughening/ion exchange. This property can be calculated by examining the depth of the ion-exchanged layer (DoL in μm) upon ion exchange after a certain ion exchange time (IET in hours). The higher the diffusivity, the deeper the DoL after a given time of ion exchange. The corresponding formula is $D = \frac{DoL^2}{7.84 \cdot IET}$. In this disclosure, if nothing else is indicated, any indication of D relates to chemical toughening with an alkali nitrate salt (100%) for 30 minutes, wherein for small glass thicknesses the duration of chemical toughening can be reduced, e.g., to 15 minutes. The temperature may be chosen at 380°C for sodium nitrate baths, and at 440°C for the other alkali nitrates. The alkali nitrate is the nitrate of the alkali metal ion that has the next larger diameter compared to the most abundant alkali metal oxide in the glass composition. The diameters of the alkali metal ions are $Cs > K > Na > Li$, e.g., if the most abundant alkali metal oxide in the glass is sodium, D is indicated for ion exchange with 100% KNO_3 at 440°C for 30 minutes.

Central tension (CT): When CS is induced on one side or both sides of a glass sheet, to balance the stress according to the 3rd principle of Newton’s law, a tension stress must be induced

in the center region of glass, and it is called central tension. CT can be calculated from measured CS and DoL.

As used herein “surface roughness” relates to the average roughness R_a , which is a measure of the texture of a surface. Commonly, amplitude parameters characterize the surface based on the vertical deviations of the roughness profile from the mean line. R_a is the arithmetic average of the absolute values of these vertical deviations. It can be determined according to DIN EN ISO 4287:2010-07.

Warp is the difference between the maximum and minimum distances of the median surface of a free, unclamped glass article from a reference plane. The warp may be measured as described in SEMI MF1390.

The total thickness variation (TTV) is the difference between the highest thickness and the lowest thickness of a glass article. It may be measured as described in SEMI MF1530.

“Hydrolytic resistance” relates to the extracted Na_2O equivalent. It is determined in accordance with ISO 719:2020-09. It is a measure of the extractability of the basic compounds from the glass in water at 98°C . The result of the measurement is the extracted Na_2O equivalent in μg per g of glass.

“Alkali resistance” relates to the resistance of a glass to alkaline attack. It is determined according to ISO 695:1991-05 using a boiling aqueous solution of sodium carbonate and sodium hydroxide. The test is performed as described under section 6.2 “glass as a material”. The result is the loss in mass per surface area of the glass sample in mg/dm^2 .

“Acid resistance” relates to the resistance of a glass to acid attack. It is determined according to DIN 12116:2001-03 using a boiling aqueous solution of hydrochloric acid. The test is performed as described under section 6.3 “glass as a material”. The result is the loss in mass per surface area of the glass sample in mg/dm^2 .

“ T_4 ” is the temperature at which the glass has a viscosity of $10^4 \text{ dPa}\cdot\text{s}$. T_4 can be measured by methods known to a person skilled in the art for determining the viscosity of glass, e.g., in accordance with ISO 7884-2:1987-12. “ T_{13} ” is the temperature at which the glass has a viscosity of $10^{13} \text{ dPa}\cdot\text{s}$. Similarly, other temperatures indicated as T_n refer to the temperature where the glass has a viscosity of $10^n \text{ dPa}\cdot\text{s}$. For example, “ T_5 ” is the temperature at which the glass has a viscosity of $10^5 \text{ dPa}\cdot\text{s}$. The “strain point” ($T_{14.5}$) is defined as a temperature at which all movement of the glass molecules has reached a point at which no more strain can be introduced into the hot glass. It is a viscosity fixed point (temperature value) at the viscosity $\eta = 10^{14.5} \text{ dPa}\cdot\text{s}$.

This limit represents the highest service temperature of a glass component. “T_g” is the transformation temperature according to ISO 7884-8:1987.

Three-point bending strength is a test of the flexural strength of a material. It may be determined using the method described in ASTM C1161-13. An exemplary test setup is as follows: Cylindrical steel bearings of 2 mm radius; support span 16 mm; specimens of size 28*28*0.2 mm³; prepared according to Standard procedure 7.2.4; loading speed of 5 mm/min.

Vickers Hardness was determined using a standard Vickers indenter as specified in ASTM C 1327 (2015). The following parameters were used: force F_n (max) = 1 N; approximation speed = 4 μm/min; loading rate 2 N/min; holding time 20 s; release rate 6 N/min.

Typically, the Vogel-Fulcher-Tammann (VFT) equation is used to calculate the temperature needed to achieve a certain viscosity of a glass (see the ISO 7884 series of standards e.g. ISO 7884-1:1987-12, 7884-2:1987-12; 7884-3:1987-12; 7884-4:1987-12):

$$\lg \eta = A + \frac{B}{T - T_0}$$

In the VFT equation, η is the viscosity, A and B are parameters of the material, T is the temperature and T₀ is the Vogel temperature. A, B and T₀ are constant for any specific glass. The indication of these constants provides for a more detailed information about the viscosity behavior of a certain glass composition.

“Major surfaces” of an article are the two surfaces having the largest areas among all surfaces of the article.

When in this disclosure it is mentioned that the glasses are “free of a component” or that they do not contain a certain component, then this means that this component is only allowed to be present as an impurity in the glasses. This means that it is not added in substantial amounts. Not substantial amounts are amounts of less than 3000 ppm (by weight), less than 2500 ppm (by weight), less than 2000 ppm (by weight), less than 1500 ppm (by weight), less than 1250 ppm (by weight), particularly less than 750 ppm (by weight) or less than 500 ppm (by weight).

The terms “chemical toughening” and “chemical strengthening” are used interchangeably hereinunder.

Compositional aspects

It was found that within the compositional matrix of this disclosure, the disclosed compositions, ratios and sum of contents provide for an improved susceptibility to chemical strengthening, maintaining devitrification resistance, and good chemical resistance (in particular acid resistance). Optionally, the glass compositions as disclosed herein may essentially consist of the listed oxides, i.e. being free of any other components not mentioned in this disclosure.

In one embodiment, the glass comprises the following components:

- i. SiO_2 ,
- ii. Al_2O_3 in an amount of 0.0 to 6.0% by weight,
- ii. ZrO_2 in an amount of at least 8.0% by weight,
- iii. Na_2O in an amount of at least 12.0% by weight,
- iv. 0.0 to 5.0% by weight of B_2O_3
- v. 0.0 to 5.0% by weight of Li_2O ,
- vi. 0.0 to 10.0% by weight of K_2O ; and
- vii. optionally, one or more components selected from P_2O_5 and TiO_2 .

Optionally, the glass comprises the following components in percent by weight:

SiO_2	40.0 to 70.0
Al_2O_3	0.0 to 6.0
Na_2O	12.0 to 25.0
ZrO_2	8.0 to 32.0
B_2O_3	0.0 to 5.0
Li_2O	0.0 to 5.0
K_2O	0.0 to 10.0
MgO	0.0 to 20.0
CaO	0.0 to 15.0
$\text{MgO}+\text{CaO}$	at least 1.5
SrO	0.0 to 10.0
BaO	0.0 to 10.0
ZnO	0.0 to 10.0

P ₂ O ₅	0.0 to 10.0
TiO ₂	0.0 to 5.0
Y ₂ O ₃	0.0 to 20.0
La ₂ O ₃	0.0 to 10.0
Nb ₂ O ₅	0.0 to 10.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

and, optionally, comprising a dye or colorant, such as Fe₂O₃, CoO, and/or Cr₂O₃.

It was found that ZrO₂ may be present in amounts of at least 8.0% by weight and Al₂O₃ should be kept below 6.0% by weight to achieve the desired CSS, devitrification and acid resistance properties.

In an embodiment, the glass comprises

SiO ₂	46.0 to 65.0
Al ₂ O ₃	0.0 to 3.0
Na ₂ O	15.0 to 19.0
ZrO ₂	12.0 to 30.0

In one embodiment, the ratio of the amount of ZrO₂ to the amount of Al₂O₃ in percent by weight is at least 1.5. In yet another embodiment that ratio may be at least 2, at least 3, at least 4, at least 5, at least 10, at least 20, at least 30, at least 50, at least 65, at least 75, at least 100, at least 125, or even at least 130. Optionally, this ratio may be up to 200, up to 180, up to 150, up to 125, up to 110, or up to 75. For example, this ratio may be from 1.5 to 200, from 2 to 150, from 5 to 145, from 10 to 135. This ratio may include also glasses substantially free of Al₂O₃, i.e., only comprising Al₂O₃-impurities or being completely free of Al₂O₃, wherein the ratio tends towards infinity.

In an embodiment, the ratio of the amount of Al₂O₃ to the amount of ZrO₂ in percent by weight is less than 0.5, less than 0.25, less than 0.20, less than 0.15, less than 0.10, less than 0.05, less than 0.025, or even less than 0.015. Optionally, this ratio may be at least 0.001, at least 0.0025, at least 0.005, or at least 0.0065. For example, this ratio may be from 0.001 to 0.5, from 0.0025 to 0.2, from 0.005 to 0.1, from 0.0065 to 0.025. This ratio may include also glasses substantially free of Al₂O₃, i.e., only comprising Al₂O₃-impurities or being completely free of Al₂O₃, wherein the ratio tends towards 0.0.

In certain embodiments, the sum of the contents of Al_2O_3 and ZrO_2 is from 8.0% by weight to 35.0% by weight, from 10.0% by weight to 33.0% by weight, or from 12.0% by weight to 29.0% by weight. However, the combination of both components in high proportions leads to an increased tendency to devitrify, so that the glass cannot be manufactured using the down draw method. Therefore, the disclosed glasses may have a very small Al_2O_3 content or are free of Al_2O_3 , so that a higher proportion of ZrO_2 can be dissolved in the glass.

The glass of this disclosure may comprise ZrO_2 , Al_2O_3 and B_2O_3 . Thus, when also B_2O_3 is present, the ratio of the amount by weight of ZrO_2 to the sum of the amounts by weight of Al_2O_3 and B_2O_3 may be at least 1.5. In yet another embodiment that ratio may be at least 2, at least 3, at least 4, or even at least 5. Optionally, the ratio of the amount by weight of ZrO_2 in weight percent to the sum of the contents of Al_2O_3 and B_2O_3 in weight percent is from 1.50 to 200.00, such as from 2.00 to 180, from 2.50 to 155, from 3.65 to 145 or from 4.75 to 135. In embodiments, this ratio is at least 1.50, at least 2.00, at least 3.50, at least 4.65, or at least 5.00. This ratio may be up to 200.00, up to 180.00, up to 150.00, up to 125.00, up to 110.00, or up to 75.00. This ratio may include also glasses substantially free of Al_2O_3 and/or B_2O_3 , i.e., only comprising Al_2O_3 and/or B_2O_3 -impurities or being completely free of Al_2O_3 and/or B_2O_3 , wherein the ratio tends towards infinity.

It is important to note that conventional ZrO_2 -rich glasses in the prior art necessitate a fining step with As_2O_3 and/or Sb_2O_3 . This is harmful to the environment and health. The disclosed glasses can be produced without the use of As_2O_3 and/or Sb_2O_3 and still maintain high quality. Fining of the disclosed glasses may be carried out using CeO_2 , SnO_2 , Cl , or SO_3 , or any combination thereof. In one embodiment the glasses may not need fining by fining agents. Thus, in one embodiment, the fining is carried out without the use of harmful substances, such as As_2O_3 and/or Sb_2O_3 and therefore, in one embodiment, the glass composition is free of As_2O_3 and/or Sb_2O_3 . In this case the term “free of As_2O_3 and/or Sb_2O_3 ” refers to an amount of 100 ppm by weight or less, 50 ppm by weight or less, 25 ppm by weight or less, 20 ppm by weight or less, 10 ppm by weight or less, 5 ppm by weight or less, or even 1 ppm by weight or less.

In some embodiments, the glass is free of Li_2O . High Li_2O contents lead to increased raw material costs, which can be avoided by the disclosed glasses.

In this disclosure, the alkali metal oxides R_2O include the oxides of lithium, sodium, potassium and cesium. In some embodiments, the glass is free of lithium, potassium and/or cesium. The alkali earth metal oxides $\text{R}'\text{O}$ include the oxides of magnesium, calcium, strontium and barium. In some embodiments, the glass is free of magnesium, calcium, cesium, strontium and/or barium.

Hereinunder R_2O is the sum of the amounts of the alkali metal oxides and $R'O$ is the sum of the amounts of all alkali earth metal oxides. In some embodiments, the glass has a sum of the amounts of alkali metal oxides (R_2O), alkali earth metal oxides ($R'O$) and ZnO of not more than 35.0% by weight, not more than 34.0% by weight, or not more than 33.75% by weight. Optionally, this sum $R_2O+R'O+ZnO$ is at least 19.0% by weight, at least 20.0% by weight, or at least 21.0% by weight. For example, the sum $R_2O+R'O+ZnO$ is from 19.0 to 35.0% by weight, from 20.0 to 34.0% by weight, or from 21.0 to 33.75% by weight.

In embodiments, the glass has a sum of the amounts of alkali earth metal oxides ($R'O$) and ZnO of not more than 12.5% by weight, not more than 12.0% by weight, not more than 11.5% by weight, not more than 11.0% by weight, not more than 10.5% by weight, not more than 10.0% by weight, not more than 9.5% by weight, not more than 9.0% by weight, not more than 8.5% by weight, or not more than 8.25% by weight. Optionally, this sum $R'O+ZnO$ is at least 0.1% by weight, at least 0.5% by weight, at least 0.75% by weight, at least 1.0% by weight, or at least 1.9% by weight. For example, the sum $R'O+ZnO$ is from 0 to 12.5% by weight, from 0 to 11.5% by weight, from 0 to 10.5% by weight, from 0 to 9.5% by weight, from 0 to 8.5% by weight, from 0.1 to 11.0% by weight, from 0.5 to 10.0% by weight, from 1.0 to 9.0% by weight, from 1.5 to 8.5% by weight, or from 1.9 to 8.25% by weight.

The glass may comprise one or more alkali metal oxides (R_2O). Optionally, a ratio of a second most abundant alkali metal oxide B, and a most abundant alkali metal oxide A in weight percent is less than 0.23, less than 0.22, less than 0.18, less than 0.16, less than 0.12, or less than 0.10. The "most abundant" alkali metal oxide is the one that has the highest proportion in the glass based on weight percentage. Accordingly, the "second most abundant" is the one having the second highest proportion on a weight percent basis and so on. In an embodiment, A is Na_2O , and B is K_2O , in an alternative embodiment B is Na_2O and A is K_2O . In certain embodiments, this ratio may be as low as 0.10 or less, 0.05 or less or even 0.04 or less. In some cases, this ratio may be 0.

In an embodiment, the glass composition has a ratio of the weight amount of K_2O relative to the sum of the weight amounts of Li_2O and Na_2O of less than 0.23, less than 0.22, less than 0.18, less than 0.16, less than 0.12, or less than 0.10. In certain embodiments, this ratio may be as low as 0.10 or less, 0.05 or less or even 0.04 or less. In some cases, this ratio may be 0.

In an alternative embodiment, a ratio of the weight amount of Na_2O relative to the sum of the weight amounts of Li_2O and K_2O of less than 0.23, less than 0.22, less than 0.18, less than 0.16, less than 0.12, or less than 0.10. In certain embodiments, this ratio may be as low as 0.10 or less, 0.05 or less or even 0.04 or less. In some cases, this ratio may be 0.

In an embodiment, the glass has a ratio of the weight amount of SiO_2 relative to the sum of the weight amounts of Li_2O and Na_2O of less than 4.5, optionally less than 4.25, or less than 4.0. Optionally, this ratio may be at least 2.0, at least 2.5, or at least 3.0. For example, this ratio may range from 2.0 to 4.5, from 3.0 to 4.25, or from 3.0 to 4.0. The inventors found that this ratio has a positive influence on the thermal expansion and CSS properties of the glass.

The glass contains SiO_2 , optionally in amounts of at least 40.0% by weight, at least 41.0% by weight, at least 43% by weight, at least 45% by weight, or at least 48% by weight. In embodiments, the content of SiO_2 is up to 70.0% by weight, up to 68.0% by weight, up to 66.0% by weight or up to 64.0% by weight. In certain embodiments, the relative amount of this component is from 40.0 to 70.0% by weight, from 41.0 to 68.0% by weight, from 43.0 to 66.0% by weight or from 48.0 to 65.0% by weight. SiO_2 helps to achieve the desired thermal expansion behavior and the chemical resistance property. If the SiO_2 content is too large, viscosity increases raising the temperatures of melting and hot forming. Furthermore, SiO_2 decreases ion exchangeability and with this decreasing compressive stress at the surface.

Low Al_2O_3 -amounts may be used to help achieving the desired acid resistance. However, excessive Al_2O_3 -contents in the disclosed glass may lead to devitrification. Thus, optionally, the amount of this component is at least 0.1 % by weight, at least 0.25% by weight, at least 0.5% by weight, at least 0.75% by weight, at least 1.25% by weight, at least 1.5% by weight, at least 1.75% by weight, or at least 1.8% by weight. In embodiments, the content of Al_2O_3 may be limited to up to 5.0% by weight, up to 4.5% by weight, up to 4.0% by weight, up to 3.5% by weight, up to 3.0% by weight, up to 2.5% by weight, or up to 2.0% by weight. For example, the content of this oxide may range from 0.1 to 5.0% by weight, from 0.25 to 4.5% by weight, from 0.5 to 4.0% by weight, from 0.75 to 3.5% by weight, from 1.0 to 3.0% by weight, from 1.25 to 2.5% by weight, or from 1.5 to 2.0% by weight. However, Al_2O_3 contributes to lowering the acidic resistance of the glass and increases the viscosity of the glass. In addition, a glass melt with a high Al_2O_3 and high ZrO_2 content tends to devitrify, thus, Al_2O_3 -amounts of more than 6.0% by weight should be avoided. In some embodiments the glass may be free of Al_2O_3 .

The glass may contain B_2O_3 in proportions of up to 5.0% by weight, up to 4.5% by weight or up to 3.0% by weight. In some embodiments, the content of this component is as low as 0.75% by weight or less, 0.5% by weight or less, or even 0.25% by weight or less. Some embodiments contain less than 0.1% by weight of B_2O_3 . If present, B_2O_3 helps balance any devitrification tendency that might arise from the use of ZrO_2 . Optionally, the content of B_2O_3 ranges from 0 to 5.0% by weight, from 0 to 4.5% by weight or from 0 to 3.0% by weight. In some embodiments, B_2O_3 is used in an amount of at least 0.25% by weight, or at least 0.5% by weight. A too high

proportion of B_2O_3 , however, impairs chemical toughening performance, especially for short incubation times, thus, B_2O_3 -amounts of more than 5.0% by weight should be avoided. In some embodiments the glass may be free of B_2O_3 .

The glass may comprise Al_2O_3 and/or B_2O_3 in a total amount of from 0.0 to 10.0% by weight, provided that the ratio of the amount by weight of ZrO_2 to the sum of the amounts by weight of Al_2O_3 and B_2O_3 is at least 1.5. Optionally, the glass may comprise Al_2O_3 and/or B_2O_3 in a total amount of from 0.0 to 9.5% by weight, from 0.0 to 9.0% by weight, or from 0.0 to 8.5% by weight provided that the ratio of the amount by weight of ZrO_2 to the sum of the amounts by weight of Al_2O_3 and B_2O_3 is at least 1.5. In an embodiment, the sum of the contents of Al_2O_3 and B_2O_3 is less than 9.5% by weight, less than 9.0% by weight, less than 8.5% by weight, less than 8.0% by weight, or less than 7.0% by weight. Optionally, the sum of the contents of Al_2O_3 and B_2O_3 is at least 0.5% by weight, at least 0.75% by weight, at least 1.0% by weight, at least 1.25% by weight, or at least 1.5% by weight. In some embodiments the glass may be free of Al_2O_3 and B_2O_3 .

P_2O_5 is an optional component. It may be used in proportions of at least 0.015% by weight, at least 0.02% by weight, at least 0.025% by weight or at least 0.03% by weight. Suitable upper limits are 10.0% by weight, 8.0% by weight, 6.0% by weight, 5.0% by weight, 4.0% by weight and 3.5% by weight. Optionally, P_2O_5 may be used in ranges from 0 to 10.0% by weight, from 0.02 to 8.0% by weight, from 0.025 to 5.0% by weight, or from 0.03 to 3.5% by weight.

Some embodiments include TiO_2 as a glass component. It may be used in amounts of from 0.0 to 5.0% by weight, from 0.0 to 4.0% by weight, from 0.0 to 3.0% by weight, from 0.0 to 2.0% by weight, from 0.0 to 1.5% by weight, from 0.0 to 1.0% by weight, or in amount of less than 100 ppm.

ZrO_2 is an important component in the glass composition. It was found that ZrO_2 should be present in amounts of at least 8.0% by weight and Al_2O_3 needs to be kept below 6.0% by weight in order to achieve the desired resistance to devitrification. Desirably, the amount of ZrO_2 is at least 8.0% by weight, at least 9.5% by weight, at least 10.0% by weight, at least 10.5% by weight, at least 11.0% by weight. In some embodiments, the amount of ZrO_2 may be at least 8.1% by weight, at least 8.5% by weight, at least 8.8% by weight, at least 9.2% by weight, or at least 9.5% by weight. In embodiments, the amount of this component ranges up to 32.0% by weight, or up to 30% by weight. Optionally, the content of ZrO_2 in the glass may range from 8.0 to 32.0% by weight, from 9.5 to 32.0% by weight, from 10.0 to 30.0% by weight, from 10.5 to 20.0% by weight, from 11.0 to 17.5% by weight, from 8.1 to 28.0% by weight, from 8.5 to 24.0% by weight, from 8.8 to 23.5% by weight, or from 9.5 to 22.5% by weight. In an embodiment, the

amount of ZrO_2 is at least 8.5% by weight, at least 8.7% by weight, or at least 9.0% by weight. In certain embodiments, the amount of ZrO_2 may be at least 8.0% by weight, at least 9.0% by weight, or >10.0% by weight, such as at least 10.1% by weight. Thus, in an embodiment, the amount of ZrO_2 may range from 8.0% by weight to 30.0% by weight. ZrO_2 is an essential component to increase compressive stress at the surface after ion exchange due to increasing packing density. It further improves chemical resistance and decreases CTE. However, it was found that if ZrO_2 is too high, meltability deteriorates and devitrification as well as phase separation can occur which lowers yield.

In some embodiments Y_2O_3 may be present in the glass composition. The amount of Y_2O_3 may be at least 5.0% by weight, at least 6.0% by weight, at least 7.0% by weight, or at least 8.5% by weight. In embodiments, the amount of this component ranges up to 20.0% by weight, up to 15.0% by weight, up to 10.0% by weight, or up to 5.0% by weight. Optionally, the content of Y_2O_3 in the glass may range from 0.0 to 20.0% by weight, from 0.0 to 15.0% by weight, from 0.0 to 10.0% by weight, or from 0.0 to 5.0% by weight. In some embodiments the glass may be free of Y_2O_3 .

In certain embodiments, the ratio of (a) the content of ZrO_2 in weight percent to (b) the content of SiO_2 in weight percent is from 0.10 to 0.75, from 0.15 to 0.70 or from 0.19 to 0.65. In an embodiment, this ratio is at least 0.08, at least 0.10, at least 0.15 or at least 0.19. This ratio may range up to 0.70, up to 0.68, up to 0.65, up to 0.625, or up to 0.62.

Optionally, the glass comprises alkali metal oxides. The total amount of alkali metal oxides R_2O may be from 10.0 to 30.0% by weight. Optionally, this amount is at most 25.0% by weight, at most 23.0% by weight, at most 22.0% by weight, at most 21.0% by weight, or at most 20.5% by weight. A certain amount of alkali metal oxides may be necessary for a sufficient CSS property. Hence, a minimum amount may be 10.0% by weight, 11.0% by weight, 12.0% by weight, or even 13.0% by weight. For example, the R_2O amount may range from 10.0 to 25.0% by weight, from 11.0 to 24.0% by weight, from 11.0 to 23.0% by weight, or from 12.0 to 22.0% by weight. In certain embodiments, the sum of the contents of all alkali metal oxides R_2O is less than 20.5% by weight, less than 20.25% by weight, or less than 20.15% by weight.

Optionally, the ratio of (a) the sum of the contents of all alkali metal oxides R_2O in weight percent to (b) the content of SiO_2 in weight percent is from 0.1 to <0.4, from 0.15 to <0.39, from 0.2 to <0.38 or from 0.25 to <0.37.

In an embodiment, the most abundant alkali metal oxide in the glass composition is Na_2O , the second most abundant alkali metal oxide, if present, is in some embodiments K_2O , in other embodiments Li_2O , and the third most abundant alkali metal oxide, if present, is in some embodiments Li_2O , in other embodiments K_2O . Alternatively, the most abundant alkali metal oxide maybe K_2O , the second most abundant alkali metal oxide, if present, may be Na_2O , and the third most abundant alkali metal oxide, if present, may be Li_2O . In an embodiment, Li_2O is not the most abundant alkali metal oxide. Optionally, either Na_2O or K_2O is the most abundant alkali metal oxide. For example, Li_2O may be less abundant than Na_2O and/or less abundant than K_2O . Na_2O acts as network former and is an important component to ensure high compressive stress after ion exchange. It further decreases temperatures for melting and hot forming. However, if Na_2O content is too high, hydrolytic resistance will decrease dramatically.

Li_2O may be present in the glass in amounts of up to 5.0% by weight, up to 3.0% by weight, up to 2.5% by weight, up to 2.25% by weight, up to 2.15% by weight, up to 2.1% by weight, up to 1.5% by weight, up to 1.0% by weight, up to 0.5% by weight, up to 0.2% by weight, or up to 0.1% by weight. High Li_2O contents increase the costs of raw material due to the increasing demand for Li_2O for battery production, thus, Li_2O should be kept low and Li_2O of more than 5.0% by weight should be avoided. In some embodiments, the glass may be free of Li_2O .

K_2O may be present in the glass in amounts of up to 7.0% by weight, up to 6.0% by weight, or up to 5.0% by weight. In some embodiments, the content of K_2O may be at least 4.0% by weight, or at least 3.0% by weight. In an embodiment, the glass composition comprises K_2O in an amount of 5.0% by weight or less, 4.5% by weight or less, 4.0% by weight or less, 3.5% by weight or less, 3.0% by weight or less, 2.8% by weight or less, 2.5% by weight or less, 2.0% by weight or less, or 1.5% by weight or less. It may alternatively be used in proportions of at least 1.0% by weight, at least 2.0% by weight or at least 3.0% by weight. However, too much K_2O in the glass will reduce the susceptibility to chemical toughening because the network is too open, thus, K_2O of more than 10.0% by weight should be avoided. In some embodiments, the glass may be free of K_2O .

Na_2O may be present in the glass in amounts of up to 22.0% by weight, up to 20.0% by weight, or up to 19.0% by weight. In some embodiments, the content of Na_2O may be at least 14.0% by weight, or at least 15.0% by weight.

Optionally, the total amount of Na_2O and/or K_2O may range from 10.0 to 22.0% by weight, from 14.0 to 21.0% by weight, or from 15.0 to 20.5% by weight.

A total amount of up from 10.0 to 40.0% by weight of one or more oxides selected from ZnO, Li₂O, Na₂O, K₂O, MgO, CaO, SrO, BaO, and combinations thereof, may be present in the glass. In most embodiments, this total amount will be less than 30.0% by weight, less than 25.0% by weight, or less than 22.0% by weight.

The amount of CaO in the glass may for example be at most 15.0% by weight, at most 13.5% by weight, at most 12.2% by weight, at most 6.0% by weight, at most 3.0% by weight, at most 0.5% by weight, at most 0.2% by weight, or at most 0.1% by weight. If the CaO content is too high, it can reduce susceptibility to chemical strengthening, thus, CaO amounts of more than 15.0% by weight should be avoided. The glass may also be free of CaO.

The amount of SrO in the glass may for example be at most 10.0% by weight, at most 7.0% by weight, at most 6.0% by weight, at most 5.0% by weight, at most 1.0% by weight, at most 0.5% by weight, at most 0.2% by weight, or at most 0.1% by weight. The glass may also be free of SrO.

The amount of BaO in the glass may for example be at most 10.0% by weight, at most 7.0% by weight, at most 5.0% by weight, at most 2.0% by weight, at most 1.0% by weight, at most 0.5% by weight, at most 0.2% by weight, or at most 0.1% by weight. The glass may also be free of BaO.

The sum of the amounts of CaO, SrO and BaO in the glass may for example be at most 20.0% by weight, at most 15.0% by weight, at most 13.0% by weight, at most 12.0% by weight, at most 11.0% by weight, at most 5.0% by weight, at most 2.0% by weight, or at most 1.0% by weight. In some embodiments the glass may be free of CaO, SrO and BaO.

The amount of ZnO in the glass may range from 0.0 to 5.0% by weight, from 0.0 to 4.0% by weight, from 0.0 to 3.0% by weight or from 0.0 to 2.0% by weight. Some embodiments contain less than 100 ppm of ZnO. In certain embodiments, the amount of ZnO may range from 0.5 to 5.0% by weight, or from 1.0 to 4.0% by weight. In some embodiments the glass may be free of ZnO.

The total amount of the alkali earth metal oxides plus the amount of ZnO may be 0 to 15.0% by weight, 0.0 to 10.0% by weight, 0.0 to 9.0% by weight, or 0.0 to 8.0% by weight, or 0.0 to 7.0% by weight, or 0.0 to 5.0% by weight.

Optionally, the amount of the alkali earth metal oxides R'O is less than 10.0% by weight, less than 6.0% by weight, less than 4.0% by weight or less than 2.0% by weight. It may alternatively

be used in proportions of at least 1.0% by weight, at least 2.0% by weight or at least 3.0% by weight.

In an embodiment, the ratio of (a) the sum of the contents of all alkali earth metal oxides R'O in weight percent to (b) the content of SiO₂ in weight percent is from 0.00 to <0.06, from 0.01 to <0.3, <0.2, <0.1, <0.05 or <0.025. Optionally, this ratio may be >0.01, >0.02, or >0.03. For example, this ratio may be from >0.01 to <0.3, or from >0.02 to <0.2.

In some embodiments, the glass may contain MgO in amount of 0.0 to 9.0% by weight, from 0.1 to 8.5% by weight or from 0.5 to 8.0% by weight. Optionally, the amount of MgO is at least 0.1% by weight, at least 0.5% by weight, or at least 1.0% by weight, for example at least 1.5% by weight, at least 2.0% by weight or at least 3.0% by weight. MgO may be advantageous with respect to devitrification resistance. MgO also acts as network former and improves meltability. It also improves the compressive stress at the surface after ion exchange since it additionally increases packing density. However, if MgO content is too high, devitrification, especially due to reaction with refractive material could occur. Further, a too high MgO content could lead to phase separation. In some embodiments however, the glass is free of MgO.

Optionally, the sum of the contents of MgO and the second most abundant alkali metal oxide in weight percent is less than 10.0% by weight, less than 9.5% by weight or less than 9.0% by weight. In an embodiment, MgO may be used in proportions of at least 1.5% by weight, at least 2.0% by weight or at least 3.0% by weight. For example, the sum of the contents of MgO and CaO may be at least 1.5% by weight, at least 5.0% by weight, at least 7.5% by weight, at least 15.0% by weight, or at least 20% by weight.

An optional glass of this disclosure comprises the following components in percent by weight:

SiO ₂	45.0 to 70.0
Al ₂ O ₃	0.0 to 6.0
B ₂ O ₃	0.0 to 5.0
P ₂ O ₅	0.0 to 10.0
Li ₂ O	0.0 to 5.0
Na ₂ O	12.0 to 25.0
K ₂ O	0.0 to 10.0
ZrO ₂	8.0 to 32.0
MgO	0.0 to 20.0
CaO	0.0 to 15.0
MgO+CaO	at least 1.5

SrO	0.0 to 10.0
BaO	0.0 to 10.0
ZnO	0.0 to 10.0
TiO ₂	0.0 to 5.0
Y ₂ O ₃	0.0 to 20.0
La ₂ O ₃	0.0 to 10.0
Nb ₂ O ₅	0.0 to 10.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

An optional glass of this disclosure comprises the following components in percent by weight:

SiO ₂	45.0 to 68.0
Al ₂ O ₃	0.0 to 3.0
B ₂ O ₃	0.0 to 5.0
P ₂ O ₅	0.0 to 10.0
Li ₂ O	0.0 to 5.0
Na ₂ O	12.0 to 25.0
K ₂ O	0.0 to 10.0
ZrO ₂	8.0 to 32.0
MgO	0.0 to 20.0
CaO	0.0 to 15.0
MgO+CaO	at least 1.5
SrO	0.0 to 10.0
BaO	0.0 to 10.0
ZnO	0.0 to 10.0
TiO ₂	0.0 to 5.0
Y ₂ O ₃	0.0 to 20.0
La ₂ O ₃	0.0 to 10.0
Nb ₂ O ₅	0.0 to 10.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

An optional glass of this disclosure comprises the following components in percent by weight:

SiO ₂	45.0 to 68.0
Al ₂ O ₃	0.0 to 3.0
B ₂ O ₃	0.0 to 5.0

P ₂ O ₅	0.0 to 10.0
Li ₂ O	0.0 to 2.0
Na ₂ O	12.0 to 25.0
K ₂ O	0.0 to 10.0
ZrO ₂	10.0 to 32.0
MgO	0.0 to 20.0
CaO	0.0 to 15.0
MgO+CaO	at least 1.5
SrO	0.0 to 10.0
BaO	0.0 to 10.0
ZnO	0.0 to 10.0
TiO ₂	0.0 to 5.0
Y ₂ O ₃	0.0 to 20.0
La ₂ O ₃	0.0 to 10.0
Nb ₂ O ₅	0.0 to 10.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

An optional glass of this disclosure comprises the following components in percent by weight:

SiO ₂	45.0 to 68.0
Al ₂ O ₃	0.0 to 3.0
B ₂ O ₃	0.0 to 5.0
P ₂ O ₅	0.0 to 10.0
Li ₂ O	0.0 to 2.0
Na ₂ O	12.0 to 25.0
K ₂ O	0.0 to 10.0
ZrO ₂	10.0 to 32.0
MgO	0.0 to 20.0
CaO	0.0 to 15.0
MgO+CaO	at least 1.8
SrO	0.0 to 5.0
BaO	0.0 to 10.0
ZnO	0.0 to 10.0
TiO ₂	0.0 to 5.0
Y ₂ O ₃	0.0 to 20.0
La ₂ O ₃	0.0 to 10.0

Nb ₂ O ₅	0.0 to 10.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

An optional glass of this disclosure comprises the following components in percent by weight:

SiO ₂	45.0 to 68.0
Al ₂ O ₃	0.0 to 3.0
B ₂ O ₃	0.0 to 5.0
P ₂ O ₅	0.0 to 10.0
Li ₂ O	0.0 to 2.0
Na ₂ O	15.0 to 25.0
K ₂ O	0.0 to 10.0
ZrO ₂	10.0 to 32.0
MgO	0.0 to 20.0
CaO	0.0 to 15.0
MgO+CaO	at least 1.8
SrO	0.0 to 5.0
BaO	0.0 to 2.0
ZnO	0.0 to 10
TiO ₂	0.0 to 5.0
Y ₂ O ₃	0.0 to 20.0
La ₂ O ₃	0.0 to 10.0
Nb ₂ O ₅	0.0 to 10.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

An optional glass of this disclosure comprises the following components in percent by weight:

SiO ₂	45.0 to 68.0
Al ₂ O ₃	0.0 to 3.0
B ₂ O ₃	0.0 to 5.0
P ₂ O ₅	0.0 to 10.0
Li ₂ O	0.0 to 2.0
Na ₂ O	15.0 to 25.0
K ₂ O	0.0 to 5.0
ZrO ₂	10.0 to 32.0
MgO	0.0 to 20.0

CaO	0.0 to 15.0
MgO+CaO	at least 1.8
SrO	0.0 to 5.0
BaO	0.0 to 2.0
ZnO	0.0 to 10
TiO ₂	0.0 to 3.0
Y ₂ O ₃	0.0 to 20.0
La ₂ O ₃	0.0 to 10.0
Nb ₂ O ₅	0.0 to 10.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

An optional boron-containing glass of this disclosure comprises the following components in percent by weight:

SiO ₂	51.0 to 70.0
Al ₂ O ₃	0.0 to 1.0
B ₂ O ₃	1.0 to 3.0
P ₂ O ₅	0.0 to 1.0
Li ₂ O	0.0 to 1.0
Na ₂ O	14.0 to 20.0
K ₂ O	0.0 to 5.0
MgO	4.0 to 6.0
CaO	0.0 to 1.0
ZnO	0.0 to 1.0
TiO ₂	0.0 to 1.0
ZrO ₂	11.0 to 15.0
Fe ₂ O ₃	0.0 to 1.0
SnO ₂	0.0 to 1.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

An optional non-boron-containing glass of this disclosure comprises the following components in percent by weight:

SiO ₂	51.0 to 70.0
Al ₂ O ₃	0.0 to 2.0
P ₂ O ₅	0.0 to 1.0

Li ₂ O	0.0 to 1.0
Na ₂ O	14.0 to 20.0
K ₂ O	0.0 to 5.0
MgO	4.0 to 6.0
CaO	0.0 to 1.0
ZnO	0.0 to 1.0
TiO ₂	0.0 to 1.0
ZrO ₂	11.0 to 15.0
Fe ₂ O ₃	0.0 to 1.0
SnO ₂	0.0 to 1.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

An optional Al₂O₃-containing glass of this disclosure comprises the following components in percent by weight:

SiO ₂	53.0 to 73.0
Al ₂ O ₃	0.5 to 4.0
P ₂ O ₅	0.0 to 1.0
Li ₂ O	0.0 to 1.0
Na ₂ O	14.0 to 20.0
K ₂ O	0.0 to 2.0
MgO	0.0 to 6.0
CaO	0.0 to 3.0
ZnO	0.0 to 1.0
TiO ₂	0.0 to 1.0
ZrO ₂	10.0 to 16.0
Fe ₂ O ₃	0.0 to 1.0
SnO ₂	0.0 to 1.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

An optional low Al₂O₃-containing glass of this disclosure comprises the following components in percent by weight:

SiO ₂	51.0 to 69.0
Al ₂ O ₃	0.25 to 1.5
P ₂ O ₅	0.0 to 1.0

Li ₂ O	0.0 to 1.0
Na ₂ O	14.0 to 20.0
K ₂ O	0.0 to 3.0
MgO	1.0 to 5.0
CaO	0.0 to 3.0
ZnO	0.0 to 2.5
TiO ₂	0.0 to 1.0
ZrO ₂	13.0 to 18.0
Fe ₂ O ₃	0.0 to 1.0
SnO ₂	0.0 to 1.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

An optional P₂O₅-containing glass of this disclosure comprises the following components in percent by weight:

SiO ₂	51.0 to 69.0
Al ₂ O ₃	< 2000 ppm
P ₂ O ₅	1.0 to 4.0
Li ₂ O	0.0 to 1.0
Na ₂ O	14.0 to 20.0
K ₂ O	0.0 to 3.0
MgO	2.0 to 6.0
CaO	0.0 to 3.0
ZnO	0.0 to 1.0
TiO ₂	0.0 to 1.0
ZrO ₂	11.0 to 15.0
Fe ₂ O ₃	0.0 to 1.0
SnO ₂	0.0 to 1.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

An optional glass of this disclosure with relatively high K₂O comprises the following components in percent by weight:

SiO ₂	51.0 to 69.0
Al ₂ O ₃	< 1.5
P ₂ O ₅	0.0 to 1.0

Li ₂ O	0.0 to 1.0
Na ₂ O	14.0 to 20.0
K ₂ O	1.0 to 4.0
MgO	0.5 to 4.0
CaO	0.0 to 3.0
ZnO	0.0 to 2.5
TiO ₂	0.0 to 1.0
ZrO ₂	13.0 to 19.5
Fe ₂ O ₃	0.0 to 1.0
SnO ₂	0.0 to 1.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

An optional glass of this disclosure with relatively high ZrO₂ comprises the following components in percent by weight:

SiO ₂	51.0 to 69.0
Al ₂ O ₃	< 2000 ppm
P ₂ O ₅	0.0 to 1.0
Li ₂ O	0.0 to 1.0
Na ₂ O	14.0 to 20.0
K ₂ O	0.0 to 2.0
MgO	2.0 to 5.0
CaO	0.0 to 3.0
ZnO	0.0 to 1.0
TiO ₂	0.0 to 1.0
ZrO ₂	18.0 to 22.0
Fe ₂ O ₃	0.0 to 1.0
SnO ₂	0.0 to 1.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

An optional glass of this disclosure with relatively high CaO comprises the following components in percent by weight:

SiO ₂	51.0 to 69.0
Al ₂ O ₃	< 2000 ppm
P ₂ O ₅	0.0 to 1.0

Li ₂ O	0.0 to 1.0
Na ₂ O	14.0 to 20.0
K ₂ O	0.0 to 2.0
MgO	0.0 to 2.0
CaO	5.0 to 9.0
ZnO	0.0 to 1.0
TiO ₂	0.0 to 1.0
ZrO ₂	11.0 to 15.0
Fe ₂ O ₃	0.0 to 1.0
SnO ₂	0.0 to 1.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

An optional glass of this disclosure with relatively high MgO comprises the following components in percent by weight:

SiO ₂	45.0 to 67.0
Al ₂ O ₃	< 3.5
P ₂ O ₅	0.0 to 1.0
Li ₂ O	0.0 to 2.0
Na ₂ O	14.0 to 20.0
K ₂ O	0.0 to 2.5
MgO	3.5 to 8.5
CaO	0.0 to 3.0
ZnO	0.0 to 1.0
TiO ₂	0.0 to 1.0
ZrO ₂	13.0 to 15.0
Fe ₂ O ₃	0.0 to 1.0
SnO ₂	0.0 to 1.0
SO ₃	0.0 to 1.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

Another optional glass of this disclosure with relatively high ZrO₂ comprises the following components in percent by weight:

SiO ₂	45.0 to 67.0
Al ₂ O ₃	< 3.5

P ₂ O ₅	0.0 to 1.0
Li ₂ O	0.0 to 1.0
Na ₂ O	14.0 to 20.0
K ₂ O	0.0 to 2.0
MgO	3.5 to 8.5
CaO	0.0 to 3.0
ZnO	0.0 to 1.0
TiO ₂	0.0 to 1.0
ZrO ₂	20.0 to 32.0
Fe ₂ O ₃	0.0 to 1.0
SnO ₂	0.0 to 1.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

The glass may comprise one or more fining agents, such as CeO₂, SnO₂, Cl, SO₃. Fe₂O₃ may optionally be used as fining aid. Therefore, the glass may optionally comprise Fe₂O₃. It is desirable to avoid the toxic fining agent's arsenic and antimony, so that the sum of the amounts of arsenic and antimony may be less than 100 ppm. Due to toxicity concerns, the sum of the amounts of lead and bismuth may be less than 100 ppm. In embodiments, the glass may contain F in amounts of less than 1% by weight.

In one embodiment, the glass may comprise coloring ions as dyes and/or colorants, such as iron, cobalt, chromium, copper, vanadium, nickel, manganese, neodymium, erbium, europium, molybdenum or combinations thereof. They may be used in their various oxidation states.

In one embodiment, in order to improve the meltability in this glass system further, B₂O₃, K₂O, MgO and/or CaO may be used.

Parameters

A coefficient of thermal expansion of the glass may be less than $9.8 \times 10^{-6} \text{ K}^{-1}$, less than $9.7 \times 10^{-6} \text{ K}^{-1}$ or less than $9.6 \times 10^{-6} \text{ K}^{-1}$. In exceptional embodiments the coefficient of thermal expansion is up to $10.0 \times 10^{-6} \text{ K}^{-1}$, up to $9.5 \times 10^{-6} \text{ K}^{-1}$, or up to $9.2 \times 10^{-6} \text{ K}^{-1}$. Optionally, the coefficient of thermal expansion is at least $7.0 \times 10^{-6} \text{ K}^{-1}$, at least $7.5 \times 10^{-6} \text{ K}^{-1}$, or at least $8.0 \times 10^{-6} \text{ K}^{-1}$, or at least $8.2 \times 10^{-6} \text{ K}^{-1}$. In embodiments, the coefficient of thermal expansion of the glass ranges from $7.0 \times 10^{-6} \text{ K}^{-1}$ to $9.8 \times 10^{-6} \text{ K}^{-1}$, from $7.5 \times 10^{-6} \text{ K}^{-1}$ to $9.7 \times 10^{-6} \text{ K}^{-1}$, or from $8.0 \times 10^{-6} \text{ K}^{-1}$ to $9.6 \times 10^{-6} \text{ K}^{-1}$, or from $8.2 \times 10^{-6} \text{ K}^{-1}$ to $9.6 \times 10^{-6} \text{ K}^{-1}$. In certain embodiments, the coefficient of thermal expansion is less than $9.59 \times 10^{-6} \text{ K}^{-1}$ or even less than $9.58 \times 10^{-6} \text{ K}^{-1}$.

The glass may have a Young's modulus of at least 74 GPa, at least 75 GPa, at least 76 GPa, or at least 77 GPa. Optionally, the Young's modulus is up to 90 GPa, up to 88 GPa or up to 86 GPa. In embodiments, the Young's modulus of the glass ranges from 74 GPa to 90 GPa, from 75 GPa to 88 GPa or from 76 GPa to 86 GPa. In certain embodiments, the Young's modulus is at least 76 GPa or even at least 77 GPa. The glass of this disclosure may have an excellent Young's modulus (in GPa) of between 70 and 90.

Generally, a higher Young's modulus will increase the tensile stress at the glass surface upon bending. It will also reduce a glass article's tendency to forming creases in a bending region. A high compressive stress at the surface can compensate for the tensile stress upon bending. Since the disclosed glasses show an improved susceptibility for chemical strengthening and therefore entertain a higher CSS and CS, also the Young's modulus may be higher. This has the advantage that, especially in cases of foldable display-covers, the tendency to form creases in a bending region of the display can be reduced significantly. Thus, in one embodiment the disclosed glasses are in particular suitable for foldable display-covers.

In an embodiment, the glass has a Poisson's ratio of from 0.220 to 0.270, from 0.225 to 0.265, or from 0.230 to 0.260. Optionally, Poisson's ratio may be less than 0.260, less than 0.259 or less than 0.258. In embodiments, Poisson's ratio is at least 0.220, at least 0.225 or at least 0.230.

Optionally, the glass has a density of from 2.530 to 2.850 g/cm³, from 2.580 to 2.830 g/cm³, or from 2.600 to 2.780 g/cm³. The density may be at least 2.530 g/cm³, at least 2.580 g/cm³ or at least 2.600 g/cm³. In embodiments, the density will be up to 2.850 g/cm³, up to 2.830 g/cm³, up to 2.790 g/cm³ or up to 2.780 g/cm³.

In an embodiment, the glass has a packing density of from 0.44 to 0.58, from 0.48 to 0.56, or from 0.50 to 0.54. The density may be at least 0.44, at least 0.48 or at least 0.50. In embodiments, the density will be up to 0.58, up to 0.56, up to 0.54 or up to 0.53.

In an embodiment, the glass may have a glass transition temperature T_g of at least 545°C, at least 550°C or at least 555°C. In certain embodiments, T_g may even be at least 560°C or at least 561°C, whereas particular embodiments may even have T_g values above 565°C. Optionally, T_g may be less than 680°C, or less than 675°C. In embodiments, T_g ranges from 545°C to 680°C, from 550°C to 675°C, or from 553°C to 630°C. A high T_g allows for high temperatures during ion exchange treatment. Glasses with high T_g will relax stresses induced by ion exchange at higher temperatures less than glasses with lower T_g . Higher temperatures accelerate ion exchange processes so that ion exchange becomes more economical.

In an embodiment, the glass may have a strain point of at least 500°C, at least 525°C, at least 540°C, at least 550°C or at least 560°C. In certain embodiments, the strain point may even be at least 543°C or at least 573°C, whereas particular embodiments may even have strain point values above 580°C. Optionally, the strain point may be less than 700°C, or less than 675°C. In embodiments, the strain point ranges from 500°C to 700°C, from 525°C to 685°C, or from 540°C to 675°C. A high strain point allows for high temperatures during ion exchange treatment. Glasses with high strain point will relax stresses induced by ion exchange at higher temperatures less than glasses with lower strain point. Higher temperatures accelerate ion exchange processes so that ion exchange becomes more economical.

Optionally, the glass composition exhibits one or more of

- a temperature T_4 of at least 1065°C, at least 1075°C, at least 1080°C, at least 1085°C, at least 1095°C or at least 1100°C,
- a temperature T_3 of at least 1180°C, at least 1200°C, at least 1225°C, at least 1250°C, at least 1310°C or at least 1330°C,
- a VFT constant A of <0.00, optionally from -5.00 to -2.00,
- a VFT constant B of >5,000°C, optionally from 5,800°C to 8,000°C, and
- a VFT constant T_0 of 140 to 450°C, such as from 145 to 300°C, or up to 255°C.

The glass of this disclosure may have remarkable steepness of the temperature viscosity curve. Steepness of the curve may be quantified as the difference between the temperatures T_4 and $T_{7.6}$. For the glass of this disclosure this difference may be at least 250 K, at least 265 K, at least 280 K, or at least 285 K. Optionally, this value does not exceed 380 K, 360 K, or 340 K. For example, the difference between the temperatures T_4 and $T_{7.6}$ may range from 250 to 380 K, from 265 to 260 K, or from 280 to 340 K.

All of these parameters describe the viscosity behavior of the glass. The glass of this disclosure has rather high characteristic temperatures, making it possible to use high temperatures during ion exchange, thereby accelerating the ion exchange process.

An important property of the glass of this disclosure is its ability to build high compressive stress in very short time. The property is quantified by a CSS score – or just “CSS” – which is equivalent to the compressive stress formed in a test specimen. The further used index indicates the glass thickness used for measuring CSS. The glass compositions of this disclosure have remarkable CSS values at small glass thicknesses.

Optionally, the glass of this disclosure has a $CSS_{200\mu m}$ of at least 800 MPa, at least 950 MPa, at least 1000 MPa, at least 1050 MPa, or even at least 1070 MPa. This is a very remarkable compressive stress susceptibility, which allows for introduction of very high compressive stresses into the glass within short time. Optionally, $CSS_{200\mu m}$ ranges up to 1700 MPa, up to 1500 MPa, or up to 1400 MPa. In embodiments, $CSS_{200\mu m}$ ranges from 800 MPa to 1700 MPa, from 1000 MPa to 1500 MPa, or from 1050 MPa to 1400 MPa. Prior art glass compositions reach such high compressive stresses only after much longer ion exchange times. Often, prior art glass composition will reach compressive stresses of 1000 MPa only after more than 4 hours of ion exchange or not at all.

Optionally, the glass of this disclosure has a $CSS_{30\mu m}$ of at least 600 MPa, at least 700 MPa, at least 800 MPa, at least 850 MPa, or even at least 900 MPa. Optionally, $CSS_{30\mu m}$ ranges up to 1200 MPa, up to 1100 MPa, or up to 1000 MPa. In embodiments, $CSS_{30\mu m}$ ranges from 600 MPa to 1200 MPa, from 700 MPa to 1100 MPa, or from 800 MPa to 1000 MPa. In an embodiment, the $CSS_{30\mu m}$ score refers to the $CSS_{30\mu m}$. Prior art glass compositions do not reach such high compressive stresses at such small thicknesses.

Another way of expressing the remarkable property of this glass to accept compressive stress is the 1000 MPa IOX-time, i.e., the duration of ion exchange treatment in an alkali nitrate bath needed for the glass specimen to reach 1000 MPa of compressive stress at its surface. Optionally, the 1000 MPa IOX-time of the glass of this disclosure is less than 60 minutes, less than 30 minutes or even less than 20 minutes. In an embodiment, the 1000 MPa IOX-time refers to the IOX-time in a potassium nitrate bath.

The remarkable ability of this glass to be chemically strengthened is further illustrated with reference to its diffusivity. A high diffusivity means that the glass can receive a compressive stress layer of sufficient depth within a short time, making the production process of the glass more economical. In certain embodiments, the glass of this disclosure has a diffusivity of at least 8 $\mu m^2/h$, 10 $\mu m^2/h$, 12 $\mu m^2/h$, 14 $\mu m^2/h$, or 16 $\mu m^2/h$. Optionally, this value may range up to 45 $\mu m^2/h$, 40 $\mu m^2/h$, or 35 $\mu m^2/h$. In certain embodiments, diffusivity is from 8 to 45 $\mu m^2/h$, from 9 to 40 $\mu m^2/h$, or from 10 to 31 $\mu m^2/h$.

The glass of this disclosure may have a chemical resistance characterized by one or more of

- (a) a hydrolytic resistance value in $\mu g/g$ sodium equivalent of less than 320, or of less than 300, or of less than 280, or of less than 250, or of less than 225, or of less than 210;
- (b) an alkali resistance value in mg/dm^2 weight loss of less than 25, or of less than 22, or of less than 20, or of less than 18;

- (c) an acid resistance value in mg/dm^2 weight loss of less than 5.0, or of less than 2.5, or of less than 2.0, or less than 1.0.

Optionally, a hydrolytic resistance value in $\mu\text{g/g}$ sodium equivalent may be at least 15, at least 50, or at least 100. In an embodiment, an alkali resistance value in mg/dm^2 weight loss of is at least 1, at least 5, or at least 8. In a further embodiment, an acid resistance value in mg/dm^2 weight loss of may be at least 0.1, at least 0.2, or at least 0.3.

Glasses of this disclosure exhibit remarkable compressive stress susceptibility in MPa relative to the total content of alkali metal oxides R_2O and alkali earth metal oxides $\text{R}'\text{O}$ in weight percent $\frac{\text{CSS}_{200\mu\text{m}}}{[\text{R}_2\text{O}]+[\text{R}'\text{O}]}$. Prior art glasses need very high amounts of alkali metal oxides or alkali earth metal oxides in order to achieve compressive stress during ion exchange. To the contrary, the compositions described herein build high compressive stress even with moderate proportions of alkali metals and alkali earth metals. Optionally, $\frac{\text{CSS}_{200\mu\text{m}}}{[\text{R}_2\text{O}]+[\text{R}'\text{O}]}$ is at least 25, at least 30, at least 40, at least 50 or at least 60. In some embodiments, $\frac{\text{CSS}_{200\mu\text{m}}}{[\text{R}_2\text{O}]+[\text{R}'\text{O}]}$ is at least 70, at least 80, or at least 90. Optionally, $\frac{\text{CSS}_{200\mu\text{m}}}{[\text{R}_2\text{O}]+[\text{R}'\text{O}]}$ range up to 100, up to 75, or up to 50. In some embodiments, $\frac{\text{CSS}_{200\mu\text{m}}}{[\text{R}_2\text{O}]+[\text{R}'\text{O}]}$ is from 25 to 100, from 30 to 75, or from 35 to 65. The unit of this parameter (MPa/wt. %) is not indicated for reasons of legibility.

In an embodiment, this disclosure relates to a glass having a $\text{CSS}_{200\mu\text{m}}$ in MPa relative to the coefficient of thermal expansion in a temperature range of from 20 to 300°C in ppm/K $\frac{\text{CSS}_{200\mu\text{m}}}{\text{CTE}}$ of at least 85, at least 100, at least 110, at least 120 or at least 130. Prior art glass compositions have the drawback of high thermal expansion, often above $9.0 \times 10^{-6} \text{ K}^{-1}$. The glass compositions of this disclosure provide for high $\text{CSS}_{200\mu\text{m}}$ at low CTE, e.g., having a $\frac{\text{CSS}_{200\mu\text{m}}}{\text{CTE}}$ from 100 to 250, from 110 to 220 or from 120 to 200. For example, $\frac{\text{CSS}_{200\mu\text{m}}}{\text{CTE}}$ may range up to 250, up to 220 or up to 200. The unit of this parameter (MPa*K/ppm) is not indicated for reasons of legibility.

The refractive index of a glass used for displays should not be too high to provide for limited reflectance. Optionally, the refractive index n_d of the glass of this disclosure is less than 1.600, less than 1.550, or even less than 1.540. In certain embodiments, the refractive index ranges from 1.520 to 1.600, or from 1.530 to 1.550.

In an embodiment, the glass does not devitrify, in particular at the working point (at a viscosity of $10^4 \text{ dPa}\cdot\text{s}$). This is useful for the glass to be producible in down draw processes. In an em-

bodiment, the glass can be produced by down draw processes such as slot down-draw or over-flow fusion down draw. It is desirable that there is no devitrification at all at the working point of 10^4 dPa*s. However, at a slightly higher viscosity, in particular at a viscosity of 10^5 dPa*s, small crystal growth rates can be tolerated and glasses having crystal growth rates of not more than 0.5 $\mu\text{m}/\text{min}$ at a viscosity of 10^5 dPa*s are generally compatible with production by down draw.

Thus, for the purpose of this disclosure the devitrification resistance may be expressed in terms of crystal growth rate at a viscosity of 10^5 dPa*s. The lower the crystal growth rate is, the higher is the devitrification resistance and thus the yield. The measurement of the crystallization rate is well-known. The crystallization rate is measured along the formed crystals, i.e., at their greatest extension. In particular, the crystallization rate is determined upon subjecting the glass to gradient tempering (for example using a gradient furnace).

The so-called lower devitrification temperature (LDT) is the temperature at which devitrification starts in an increasing temperature regimen. Above the liquidus temperature (also called upper devitrification temperature (UDT)) crystals do not occur even after longer times. The values of LDT and UDT generally differ between different glasses. The terms “crystallization” and “devitrification” are used synonymously herein if not indicated otherwise.

If there is crystallization, it occurs at temperatures above the lower devitrification temperature (LDT) and below the upper devitrification temperature (UDT), thus in a range between LDT and UDT. Generally, different temperatures are tested to determine the crystal growth rates at different viscosities. This also enables determining LDT and UDT as the lower limit and upper limit, respectively, of the temperature range in which crystallization occurs.

The crystal growth rate may be determined by thermally treating the glass for a time of 16 hours in a gradient furnace with increasing temperature regimen. A gradient furnace is a furnace having different heating zones, thus a furnace having areas of different temperatures. Increasing temperature regimen means that prior to be put into the furnace the temperature of the glass is lower than the temperature in any area of the furnace. Thus, the temperature of the glass is increased by putting it into the furnace independent of which area of the furnace the glass is put into. Hence, measurement of devitrification may be done by thermal treatment for 16 hours in a (preheated) gradient furnace that has zones of different temperatures. It is a location-based gradient, not a time-based gradient, because the gradient furnace is divided into locations or zones of different temperatures.

The furnace being divided into several heating zones enables testing different temperatures (and thus different viscosities) at the same time. This is a particular advantage of a gradient furnace. The temperatures shall be chosen such that the crystallization rate can be determined at different temperatures (and thus different viscosities) in the range between LDT and UDT. If LDT and UDT are unknown, it is useful that temperatures in a relatively large range are tested in order to enable determination of LDT and UDT. For example, the lowest temperature in the gradient furnace may be chosen such that it is about 350 K below the processing temperature (working point) of the glass. The working point corresponds to a viscosity of 10^4 dPa*s.

As described above, the crystal growth rate at a viscosity of 10^5 dPa*s is of relevance with respect to the producibility by down draw processes. Optionally, the glasses of the invention are so devitrification resistant that the crystal growth rate is at most 0.5 $\mu\text{m}/\text{min}$, at most 0.4 $\mu\text{m}/\text{min}$, at most 0.3 $\mu\text{m}/\text{min}$, at most 0.2 $\mu\text{m}/\text{min}$, at most 0.1 $\mu\text{m}/\text{min}$, at most 0.05 $\mu\text{m}/\text{min}$, at most 0.02 $\mu\text{m}/\text{min}$, or at most 0.01 $\mu\text{m}/\text{min}$ at a viscosity of 10^5 dPa*s, in particular when the glass is thermally treated for 16 hours in a gradient furnace with increasing temperature regimen. In an embodiment, no devitrification occurs at all at a viscosity of 10^5 dPa*s. Importantly, if no devitrification occurs at all at a viscosity of 10^5 dPa*s, a crystal growth rate at 10^5 dPa*s cannot be determined. No devitrification at a viscosity of 10^5 dPa*s may also be expressed as a crystal growth rate of 0 $\mu\text{m}/\text{min}$.

Optionally, the crystallization rate is determined using glass grains, in particular glass grains of ca. 2 mm to 3 mm diameter. Such glass grains are put onto a carrier, such as a platinum carrier for the gradient tempering. For example, the carrier may have depressions, each for taking up a glass grain, and a hole at the bottom of each depression so that the crystallization rate can be determined microscopically. In view of the sizes of glass grains the depressions may have a diameter of 2 mm each and the holes may have a diameter of 0.9 mm each.

After the thermal treatment it can be determined microscopically which crystal growth rate occurred in which temperature range (and thus at which viscosity). The crystal growth rate at a viscosity of 10^5 dPa*s is determined based on the known correlation of temperature and viscosity. Based on the glass composition it is known which viscosity corresponds to which temperature. LDT and UDT may be determined as lower limit and upper limit, respectively, of the temperature range in which crystallization occurred. The different glass grains can easily be assigned to the different temperatures of the gradient furnace because it is known which position in the furnace has which temperature and which glass grain was located at which position in the furnace during the thermal treatment.

Toughenable article

A glass article of this disclosure may have a thickness of less than 1000 μm thickness, wherein the article comprises a glass comprising SiO_2 in an amount of at least 40.0% by weight, Na_2O in an amount of at least 12.0% by weight, further comprising ZrO_2 , wherein the ratio of the amount by weight of ZrO_2 to the sum of the amounts by weight of Al_2O_3 and B_2O_3 is at least 1.5, having a $\text{CSS}_{30\mu\text{m}}$ of at least 700 MPa and/or having an acid resistance of less than 5.0 mg/dm^2 , or an acid resistance of less than 2.5 mg/dm^2 .

A glass article of this disclosure may have a thickness of 1000 μm or less and comprise or consist of a glass as described herein. Generally, the article may be referred to as a thin glass article, or a glass sheet. It may have a thickness of less than 850 μm , less than 500 μm , less than 300 μm , less than 200 μm , or less than 100 μm . In some embodiments, the thickness may be as low as 80 μm or less, or 70 μm or less. Some articles have thicknesses of 50 μm or less, or 40 μm or less. Such thin glass articles have the property of being bendable and/or foldable. For such a flexible or foldable cover glass the desired thickness may be less than 100 μm , less than 80 μm , less than 60 μm , or less than 40 μm . In order for the article to be sufficiently impact resistant, a minimum thickness may be required. The minimum thickness may be at least 5 μm , at least 10 μm or at least 15 μm .

Owing to the remarkable property of having a low CTE and other desirable features, the glass article can be manufactured having a warp of less than 3.0 mm, less than 2.0 mm, or less than 1.0 mm. Generally, the glass article may be manufactured in a drawing process, wherein temperature differences between different portions of the glass will cause warp. Because the glass of this disclosure has a small CTE and other desirable properties, such as a good viscosity characteristic, articles with low warp may be obtained. In certain embodiments, warp is at least 5 μm , at least 10 μm , at least 100 μm , or at least 250 μm .

Optionally, the article may have a total thickness variation of less than 15 μm , less than 10 μm , less than 7 μm , or less than 5 μm . In embodiments, TTV may reach from 1 μm to 10 μm . In an embodiment, TTV is the thickness of a glass article $\pm 10.0\%$, $\pm 5.0\%$, or $\pm 3.0\%$.

The article may have an area of at least 10 cm^2 , at least 15 cm^2 , or at least 20 cm^2 . In embodiments, the article may have an area of less than 10000 cm^2 , less than 1000 cm^2 , or less than 200 cm^2 .

The article may have, on one or both of its major surfaces, a surface roughness R_a of not more than 5.0 nm, not more than 3.0 nm or not more than 1.5 nm. Such very small roughness is obtainable in a down-draw process.

The article may have, on one or both of its major surfaces, a remarkable chemical resistance. The chemical resistance may be characterized as one or more of

- (a) a hydrolytic resistance value in $\mu\text{g/g}$ sodium equivalent of less than 320, or of less than 300, or of less than 280, or of less than 250, or of less than 225, or of less than 210;
- (b) an alkali resistance value in mg/dm^2 weight loss of less than 25, or of less than 22, or of less than 20, or of less than 18;
- (c) an acid resistance value in mg/dm^2 weight loss of less than 5.0, or of less than 2.5, or of less than 2.0, or of less than 1.0.

The glass article may have a Vickers hardness of at least 580, at least 590 or at least 600. Optionally, Vickers hardness ranges from 580 to 800, from 590 to 700, or from 600 to 630.

In an embodiment, the glass article has excellent three-point bending strength, exhibiting a three-point bending strength of at least 100 MPa, at least 200 MPa or at least 300 MPa. It is remarkable that such a strength can be achieved even without ion exchange strengthening. With such high strength to start with, the strength of the article after ion exchange is even more remarkable. Optionally, the three-point bending strength may range from 100 MPa to 600 MPa, from 200 MPa to 500 MPa, or from 300 MPa to 400 MPa.

Toughened article

The glass article may comprise an ion-exchanged layer on one or both of its major surfaces. An ion exchange layer imparts high strength to the glass article. Optionally, the article may have, on one or both of its major surfaces, a compressive stress of at least 500 MPa, at least 600 MPa, at least 700 MPa, or at least 800 MPa. In embodiments, the compressive stress may range up to 1800 MPa, up to 1600 MPa, up to 1500 MPa, or up to 1400 MPa. For example, compressive stress may range from 400 MPa to 1800 MPa, from 700 MPa to 1600 MPa, or from 800 MPa to 1400 MPa.

In an embodiment, the glass article has a thickness of 20 to 40 μm , such as 25 to 35 μm and has a compressive stress on one or both of its major surfaces of at least 600 MPa, at least 700 MPa, at least 800 MPa, at least 850 MPa, or at least 900 MPa.

Optionally, the glass article exhibits a DoL on one or both of its major surfaces of from 6 to 12 μm , or from 7 to 11 μm . For example, DoL may be at least 6 μm , at least 7 μm , or at least 8 μm . Alternatively, or additionally, DoL may range up to 15 μm , up to 13 μm , up to 12 μm , or up to 11 μm .

In an embodiment, DoL is from 15 to 25% of the article thickness, or from 16 to 20% of the article thickness. In embodiments, DoL is at least 15% of the article thickness, at least 16%, or at least 17% of the article thickness. DoL may be up to 33%, up to 25%, or up to 20% of the article thickness. In this context, DoL refers to the depth of one compressive stress layer. The total DoL of all compressive stress layers may be larger.

One of the astonishing properties of the article of this disclosure is that very high compressive stress can be achieved even in thin articles. In embodiments, the glass article has, on one or both of its major surfaces, a ratio of compressive stress in MPa to article thickness in μm of at least 4.0 MPa/ μm , at least 5.0 MPa/ μm , at least 6.0 MPa/ μm or at least 10.0 MPa/ μm . In embodiments, this value may reach up to 40.0 MPa/ μm , up to 35.0 MPa/ μm , or up to 30.0 MPa/ μm . Optionally, the ratio of compressive stress in MPa to article thickness in μm is up to 10.0 MPa/ μm , up to 8.0 MPa/ μm , or up to 7.0 MPa/ μm . In certain embodiments, the ratio of compressive stress in MPa to article thickness in μm ranges from 4.0 MPa/ μm to 40.0 MPa/ μm , from 5.0 MPa/ μm to 35.0 MPa/ μm , from 5.0 MPa/ μm to 30.0 MPa/ μm or from 10.0 MPa/ μm to 29.0 MPa/ μm . In a particular embodiment, this value ranges from 20.0 MPa/ μm to 30.0 MPa/ μm . In an embodiment, the ratio of compressive stress in MPa to article thickness is at least 20.0 MPa/ μm , or at least 25.0 MPa/ μm .

Optionally, the article may have, on one or both of its major surfaces, a ratio of compressive stress in MPa to depth of ion exchanged layer in μm of at least 50 MPa/ μm , at least 75 MPa/ μm , or at least 90 MPa/ μm . In an embodiment, this value is even at least 100 MPa/ μm , at least 120 MPa/ μm or at least 140 MPa/ μm . For example, the ratio of compressive stress in MPa to depth of ion exchanged layer in μm may range from 50 to 400 MPa/ μm , from 75 to 300 MPa/ μm , or from 90 to 200 MPa/ μm . In certain embodiments, the ratio of compressive stress in MPa to depth of ion exchanged layer in μm is up to 400 MPa/ μm , up to 300 MPa/ μm or up to 200 MPa/ μm .

In an embodiment, this disclosure relates to a glass article exhibiting a three-point bending strength of at least 400 MPa, at least 500 MPa or at least 600 MPa.

In an embodiment, the glass article has excellent three-point bending strength, exhibiting a three-point bending strength of at least 400 MPa, at least 500 MPa or at least 600 MPa. It is remarkable that such a strength can be achieved. Optionally, the three-point bending strength may range from 400 MPa to 1200 MPa, from 500 MPa to 1000 MPa, or from 600 MPa to 800 MPa.

Electronic device

The glass and/or the glass article may be used in an electronic device, such as a portable computer, smartphone, tablet computer and other handheld or wearable devices. The glass and/or glass article may be part of a display.

Thus, an electronic device according to this disclosure may comprise a glass or glass article according to this disclosure. The electronic device may comprise a display, wherein the display comprises the glass and/or glass article of this disclosure. The glass article may be a cover glass of the electronic device.

The electronic device may be a flexible and/or foldable device, such as a flexible and/or foldable smartphone or tablet computer.

Method of making

The glass may be produced by melting a batch of raw materials suitable for obtaining the compositions of this disclosure. For example, the glass may be melted in a platinum crucible. After melting, the glass melt may be fined using one or more fining agents to remove bubbles. Instead of using chemical fining agents, physical fining methods such as vacuum fining can be used.

In an industrial scale, glass articles may be prepared by float or down-draw processes such as slot down-draw or overflow fusion down draw methods. Slot down-draw is preferred because it allows for very small thickness.

After forming, the article may be strengthened by ion exchange (also called “chemical strengthening”). Strengthening may include immersing the article in a bath of molten salt. The salt is selected based on the desired ion exchange process. In preferred embodiments, the salt will be an alkali salt, such as an alkali nitrate. In certain embodiments, the salt bath contains potassium nitrate, optionally, about 100% KNO_3 .

Chemically strengthening a glass article by ion exchange is well known to the skilled person. The strengthening process may be done by immersing the glass article into a salt bath which contains monovalent ions to exchange with alkali ions inside the glass. The monovalent ions in the salt bath have larger radii than alkali ions inside the glass, e.g., Na^+ , K^+ , and/or Cs^+ . A compressive stress to the glass is built up after ion exchange due to larger ions squeezing into the glass network. After ion exchange, the strength of glass is significantly improved. In addition, the CS induced by chemical strengthening improves the bending properties of the toughened

glass article and increases scratch resistance of the glass article. The typical salt used for chemical strengthening is, for example, K^+ -containing molten salt or mixtures of salts. Optional salt baths for chemical toughening are Na^+ -containing and/or K^+ -containing molten salt baths or mixtures thereof. Optional salts are $NaNO_3$, KNO_3 , $CsNO_3$, $NaCl$, KCl , $CsCl$, Na_2SO_4 , K_2SO_4 , Cs_2SO_4 , Na_2CO_3 , K_2CO_3 , Cs_2CO_3 , and $K_2Si_2O_5$. Additives such as $NaOH$, KOH and other sodium salts or potassium salts are also used to better control the rate of ion exchange for chemical strengthening. Ion exchange may for example be done in KNO_3 at temperatures in a range of from $300^\circ C$ to $480^\circ C$ or from $340^\circ C$ to $480^\circ C$, in particular from $340^\circ C$ to $450^\circ C$ or from $390^\circ C$ to $450^\circ C$. Optionally, during ion exchange the temperature of the salt bath will be in a temperature range of from T_g-400 to $T_g-100^\circ C$, or from T_g-250 to $T_g-150^\circ C$.

Chemical strengthening is not limited to a single step. It can include multi steps in one or more salt baths with alkaline metal ions of various concentrations and/or different ions in the salt baths to reach better toughening performance. Thus, the chemically toughened glass article can be toughened in one step or in the course of several steps, e.g., two steps. Two-step chemical toughening is in particular applied to Li_2O -containing glasses as lithium may be exchanged for both sodium and potassium ions.

The inventors found that the glass exhibits a very fast ion exchange and achieves high compressive stress within short times. The time during which the article is immersed within the molten salt bath at the indicated temperatures may range from 20 minutes to 12 hours, from 25 minutes to 4 hours, or from 30 minutes to 2 hours. Optionally, the time is at least 20 minutes, at least 25 minutes, or at least 30 minutes. In some embodiments, the ion exchange time is not more than 2 hours, or not more than 1 hour.

In an embodiment, the method includes:

- melting a batch of raw materials as needed to obtain a glass according to this disclosure,
- forming a glass article, such as a glass article as described herein,
- strengthening the article by ion-exchange treatment in an ion exchange bath.

Items of this disclosure

Each of the following items represents specific embodiments of glasses, glass articles, and other aspects of this disclosure, as described in detail hereinabove.

A first item relates to a glass composition, comprising

- i. SiO_2 ,
- ii. Al_2O_3 in an amount of 0.0 to 6.0% by weight,
- ii. ZrO_2 in an amount of at least 8.0% by weight,
- iii. Na_2O in an amount of at least 12.0% by weight,
- iv. 0.0 to 5.0% by weight of B_2O_3
- v. 0.0 to 5.0% by weight of Li_2O ,
- vi. 0.0 to 10.0% by weight of K_2O ; and
- vii. optionally, one or more components selected from P_2O_5 and TiO_2 .

A second item relates to a glass composition comprising the following components in percent by weight:

SiO_2	40.0 to 70.0
Al_2O_3	0.0 to 6.0
Na_2O	12.0 to 25.0
ZrO_2	8.0 to 32.0
B_2O_3	0.0 to 5.0
Li_2O	0.0 to 5.0
K_2O	0.0 to 10.0
MgO	0.0 to 20.0
CaO	0.0 to 15.0
$\text{MgO}+\text{CaO}$	at least 1.5
SrO	0.0 to 10.0
BaO	0.0 to 10.0
ZnO	0.0 to 10.0
P_2O_5	0.0 to 10.0
TiO_2	0.0 to 5.0
Y_2O_3	0.0 to 20.0
La_2O_3	0.0 to 10.0
Nb_2O_5	0.0 to 10.0
Cl	0.0 to 1.0
HfO_2	0.0 to 1.0

and, optionally, comprising a dye or colorant such as Fe_2O_3 , CoO , and/or Cr_2O_3 .

A third item relates to a glass composition comprising the following components in percent by weight:

SiO_2	45.0 to 70.0
Al_2O_3	0.0 to 6.0
B_2O_3	0.0 to 5.0
P_2O_5	0.0 to 10.0
Li_2O	0.0 to 5.0
Na_2O	12.0 to 25.0
K_2O	0.0 to 10.0
ZrO_2	8.0 to 32.0
MgO	0.0 to 20.0
CaO	0.0 to 15.0
$\text{MgO}+\text{CaO}$	at least 1.5
SrO	0.0 to 10.0
BaO	0.0 to 10.0
ZnO	0.0 to 10.0
TiO_2	0.0 to 5.0
Y_2O_3	0.0 to 20.0
La_2O_3	0.0 to 10.0
Nb_2O_5	0.0 to 10.0
Cl	0.0 to 1.0
HfO_2	0.0 to 1.0

A fourth item relates to a glass comprising the following components in percent by weight:

SiO_2	45.0 to 68.0
Al_2O_3	0.0 to 3.0
B_2O_3	0.0 to 5.0
P_2O_5	0.0 to 10.0
Li_2O	0.0 to 5.0
Na_2O	12.0 to 25.0
K_2O	0.0 to 10.0
ZrO_2	8.0 to 32.0
MgO	0.0 to 20.0
CaO	0.0 to 15.0

MgO+CaO	at least 1.5
SrO	0.0 to 10.0
BaO	0.0 to 10.0
ZnO	0.0 to 10.0
TiO ₂	0.0 to 5.0
Y ₂ O ₃	0.0 to 20.0
La ₂ O ₃	0.0 to 10.0
Nb ₂ O ₅	0.0 to 10.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

A fifth item relates to a glass comprising the following components in percent by weight:

SiO ₂	45.0 to 68.0
Al ₂ O ₃	0.0 to 3.0
B ₂ O ₃	0.0 to 5.0
P ₂ O ₅	0.0 to 10.0
Li ₂ O	0.0 to 2.0
Na ₂ O	12.0 to 25.0
K ₂ O	0.0 to 10.0
ZrO ₂	10.0 to 32.0
MgO	0.0 to 20.0
CaO	0.0 to 15.0
MgO+CaO	at least 1.5
SrO	0.0 to 10.0
BaO	0.0 to 10.0
ZnO	0.0 to 10.0
TiO ₂	0.0 to 5.0
Y ₂ O ₃	0.0 to 20.0
La ₂ O ₃	0.0 to 10.0
Nb ₂ O ₅	0.0 to 10.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

A sixth item relates to a glass comprising the following components in percent by weight:

SiO ₂	45.0 to 68.0
Al ₂ O ₃	0.0 to 3.0

B ₂ O ₃	0.0 to 5.0
P ₂ O ₅	0.0 to 10.0
Li ₂ O	0.0 to 2.0
Na ₂ O	12.0 to 25.0
K ₂ O	0.0 to 10.0
ZrO ₂	10.0 to 32.0
MgO	0.0 to 20.0
CaO	0.0 to 15.0
MgO+CaO	at least 1.8
SrO	0.0 to 5.0
BaO	0.0 to 10.0
ZnO	0.0 to 10.0
TiO ₂	0.0 to 5.0
Y ₂ O ₃	0.0 to 20.0
La ₂ O ₃	0.0 to 10.0
Nb ₂ O ₅	0.0 to 10.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

A seventh item relates to a glass comprising the following components in percent by weight:

SiO ₂	45.0 to 68.0
Al ₂ O ₃	0.0 to 3.0
B ₂ O ₃	0.0 to 5.0
P ₂ O ₅	0.0 to 10.0
Li ₂ O	0.0 to 2.0
Na ₂ O	15.0 to 25.0
K ₂ O	0.0 to 10.0
ZrO ₂	10.0 to 32.0
MgO	0.0 to 20.0
CaO	0.0 to 15.0
MgO+CaO	at least 1.8
SrO	0.0 to 5.0
BaO	0.0 to 2.0
ZnO	0.0 to 10
TiO ₂	0.0 to 5.0
Y ₂ O ₃	0.0 to 20.0

La ₂ O ₃	0.0 to 10.0
Nb ₂ O ₅	0.0 to 10.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

An eighth item relates to a glass comprising the following components in percent by weight:

SiO ₂	45.0 to 68.0
Al ₂ O ₃	0.0 to 3.0
B ₂ O ₃	0.0 to 5.0
P ₂ O ₅	0.0 to 10.0
Li ₂ O	0.0 to 2.0
Na ₂ O	15.0 to 25.0
K ₂ O	0.0 to 5.0
ZrO ₂	10.0 to 32.0
MgO	0.0 to 20.0
CaO	0.0 to 15.0
MgO+CaO	at least 1.8
SrO	0.0 to 5.0
BaO	0.0 to 2.0
ZnO	0.0 to 10
TiO ₂	0.0 to 3.0
Y ₂ O ₃	0.0 to 20.0
La ₂ O ₃	0.0 to 10.0
Nb ₂ O ₅	0.0 to 10.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

A ninth item relates to a glass comprising the following components in percent by weight:

SiO ₂	51.0 to 70.0
Al ₂ O ₃	0.0 to 1.0
B ₂ O ₃	1.0 to 3.0
P ₂ O ₅	0.0 to 1.0
Li ₂ O	0.0 to 1.0
Na ₂ O	14.0 to 20.0
K ₂ O	0.0 to 5.0
MgO	4.0 to 6.0

CaO	0.0 to 1.0
ZnO	0.0 to 1.0
TiO ₂	0.0 to 1.0
ZrO ₂	11.0 to 15.0
Fe ₂ O ₃	0.0 to 1.0
SnO ₂	0.0 to 1.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

A tenth item relates to a glass comprising the following components in percent by weight:

SiO ₂	51.0 to 70.0
Al ₂ O ₃	0.0 to 2.0
P ₂ O ₅	0.0 to 1.0
Li ₂ O	0.0 to 1.0
Na ₂ O	14.0 to 20.0
K ₂ O	0.0 to 5.0
MgO	4.0 to 6.0
CaO	0.0 to 1.0
ZnO	0.0 to 1.0
TiO ₂	0.0 to 1.0
ZrO ₂	11.0 to 15.0
Fe ₂ O ₃	0.0 to 1.0
SnO ₂	0.0 to 1.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

An eleventh item relates to a glass comprising the following components in percent by weight:

SiO ₂	53.0 to 73.0
Al ₂ O ₃	0.5 to 4.0
P ₂ O ₅	0.0 to 1.0
Li ₂ O	0.0 to 1.0
Na ₂ O	14.0 to 20.0
K ₂ O	0.0 to 2.0
MgO	0.0 to 6.0
CaO	0.0 to 3.0
ZnO	0.0 to 1.0

TiO ₂	0.0 to 1.0
ZrO ₂	10.0 to 16.0
Fe ₂ O ₃	0.0 to 1.0
SnO ₂	0.0 to 1.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

A twelfth item relates to a glass comprising the following components in percent by weight:

SiO ₂	51.0 to 69.0
Al ₂ O ₃	0.25 to 1.5
P ₂ O ₅	0.0 to 1.0
Li ₂ O	0.0 to 1.0
Na ₂ O	14.0 to 20.0
K ₂ O	0.0 to 3.0
MgO	1.0 to 5.0
CaO	0.0 to 3.0
ZnO	0.0 to 2.5
TiO ₂	0.0 to 1.0
ZrO ₂	13.0 to 18.0
Fe ₂ O ₃	0.0 to 1.0
SnO ₂	0.0 to 1.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

A thirteenth item relates to a glass comprising the following components in percent by weight:

SiO ₂	51.0 to 69.0
Al ₂ O ₃	< 2000 ppm
P ₂ O ₅	1.0 to 4.0
Li ₂ O	0.0 to 1.0
Na ₂ O	14.0 to 20.0
K ₂ O	0.0 to 3.0
MgO	2.0 to 6.0
CaO	0.0 to 3.0
ZnO	0.0 to 1.0
TiO ₂	0.0 to 1.0
ZrO ₂	11.0 to 15.0

Fe ₂ O ₃	0.0 to 1.0
SnO ₂	0.0 to 1.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

A fourteenth item relates to a glass with relatively high K₂O comprising the following components in percent by weight:

SiO ₂	51.0 to 69.0
Al ₂ O ₃	< 1.5
P ₂ O ₅	0.0 to 1.0
Li ₂ O	0.0 to 1.0
Na ₂ O	14.0 to 20.0
K ₂ O	1.0 to 4.0
MgO	0.5 to 4.0
CaO	0.0 to 3.0
ZnO	0.0 to 2.5
TiO ₂	0.0 to 1.0
ZrO ₂	13.0 to 19.5
Fe ₂ O ₃	0.0 to 1.0
SnO ₂	0.0 to 1.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

A fifteenth item relates to a glass with relatively high ZrO₂ comprising the following components in percent by weight:

SiO ₂	51.0 to 69.0
Al ₂ O ₃	< 2000 ppm
P ₂ O ₅	0.0 to 1.0
Li ₂ O	0.0 to 1.0
Na ₂ O	14.0 to 20.0
K ₂ O	0.0 to 2.0
MgO	2.0 to 5.0
CaO	0.0 to 3.0
ZnO	0.0 to 1.0
TiO ₂	0.0 to 1.0
ZrO ₂	18.0 to 22.0

Fe ₂ O ₃	0.0 to 1.0
SnO ₂	0.0 to 1.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

A sixteenth item relates to a glass with relatively high CaO comprising the following components in percent by weight:

SiO ₂	51.0 to 69.0
Al ₂ O ₃	< 2000 ppm
P ₂ O ₅	0.0 to 1.0
Li ₂ O	0.0 to 1.0
Na ₂ O	14.0 to 20.0
K ₂ O	0.0 to 2.0
MgO	0.0 to 2.0
CaO	5.0 to 9.0
ZnO	0.0 to 1.0
TiO ₂	0.0 to 1.0
ZrO ₂	11.0 to 15.0
Fe ₂ O ₃	0.0 to 1.0
SnO ₂	0.0 to 1.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

A seventeenth item relates to a glass with relatively high MgO comprising the following components in percent by weight:

SiO ₂	45.0 to 67.0
Al ₂ O ₃	< 3.5
P ₂ O ₅	0.0 to 1.0
Li ₂ O	0.0 to 2.0
Na ₂ O	14.0 to 20.0
K ₂ O	0.0 to 2.5
MgO	3.5 to 8.5
CaO	0.0 to 3.0
ZnO	0.0 to 1.0
TiO ₂	0.0 to 1.0
ZrO ₂	13.0 to 15.0

Fe ₂ O ₃	0.0 to 1.0
SnO ₂	0.0 to 1.0
SO ₃	0.0 to 1.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

An eighteenth item relates to a glass with relatively high ZrO₂ comprising the following components in percent by weight:

SiO ₂	45.0 to 67.0
Al ₂ O ₃	< 3.5
P ₂ O ₅	0.0 to 1.0
Li ₂ O	0.0 to 1.0
Na ₂ O	14.0 to 20.0
K ₂ O	0.0 to 2.0
MgO	3.5 to 8.5
CaO	0.0 to 3.0
ZnO	0.0 to 1.0
TiO ₂	0.0 to 1.0
ZrO ₂	20.0 to 32.0
Fe ₂ O ₃	0.0 to 1.0
SnO ₂	0.0 to 1.0
Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

A nineteenth item relates to a glass composition according to one of items 1 to 18, comprising SiO₂, ZrO₂, Al₂O₃ and B₂O₃, wherein the ratio of the amount by weight of ZrO₂ to the sum of the amounts by weight of Al₂O₃ and B₂O₃ is at least 1.5.

A twentieth item relates to a glass composition according to one of items 1 to 19, being free of As₂O₃ and/or Sb₂O₃

A twenty-first item relates to a glass composition according to one of items 1 to 20, wherein an amount, if at all present, of Al₂O₃, B₂O₃, Li₂O, K₂O, SrO, ZnO, SO₃, Fe₂O₃, TiO₂, SnO₂, and/or Cl, is less than 0.1% by weight, less than 500 ppm by weight, less than 200 ppm by weight, or less than 100 ppm by weight, or even about 0.0% by weight.

A twenty-second item relates to a glass composition according to one of items 1 to 21, having a coefficient of thermal expansion in a temperature range of from 20 to 300°C of less than $15.0 \times 10^{-6} \text{ K}^{-1}$, less than $12.0 \times 10^{-6} \text{ K}^{-1}$, less than $10.0 \times 10^{-6} \text{ K}^{-1}$, less than $9.8 \times 10^{-6} \text{ K}^{-1}$.

A twenty-third item relates to a glass composition according to one of items 1 to 22, having a compressive stress susceptibility defined as a $\text{CSS}_{200\mu\text{m}}$ score of at least 900 MPa.

An twenty-fourth item relates to a glass composition according to one of items 1 to 23, wherein the amount of ZrO_2 is at least 10.0%, or at least 12.0% by weight.

A twenty-fifth item relates to a glass composition according to one of items 1 to 24, wherein a ratio of the amount of ZrO_2 to the amount of Al_2O_3 in percent by weight of at least 2.0, or at least 3.0.

A twenty-sixth item relates to a glass composition according to one of items 1 to 25, having a 1000 MPa IOX-time of less than 60 minutes, or less than 30 minutes.

An twenty-seventh item relates to a glass composition according to one of items 1 to 26, having a glass transition temperature T_g of at least 540°C, at least 550°C or at least 564°C.

A twenty-eighth item relates to a glass composition according to one of items 1 to 27, the glass having a steepness of its temperature-viscosity curve characterized by a difference between its temperatures T_4 and $T_{7.6}$ of from 260 to 350 K.

A twenty-ninth item relates to a glass composition according to one of items 1 to 28, wherein the glass has a diffusivity of at least $10 \mu\text{m}^2/\text{h}$, or at least $15 \mu\text{m}^2/\text{h}$.

A thirtieth item relates to a glass composition according to one of items 1 to 29, wherein the glass has a sum of the amounts of alkali earth metal oxides and ZnO of not more than 15.0% by weight.

A thirty-first item relates to a glass composition according to one of items 1 to 30, wherein the crystal growth rate is at most $0.5 \mu\text{m}/\text{min}$ at a viscosity of $10^5 \text{ dPa}\cdot\text{s}$, when the glass is thermally treated for 16 hours in a gradient furnace with increasing temperature regimen.

A thirty-second item relates to a glass composition according to one of items 1 to 31, wherein the DoL is between 5 and $12 \mu\text{m}$.

A thirty-third item relates to a glass composition according to one of items 1 to 32, wherein the Young's modulus (in GPa) is between 70 and 90.

A thirty-fourth item relates to a glass composition according to one of items 1 to 33 comprising one or more fining agents, such as CeO_2 , SnO_2 , Cl , SO_3 or Fe_2O_3 .

A thirty-fifth item relates to a glass composition according to one of items 1 to 34 having a coefficient of thermal expansion of the glass from $7.0 \times 10^{-6} \text{ K}^{-1}$ to $9.8 \times 10^{-6} \text{ K}^{-1}$.

A thirty-sixth item relates to a glass composition according to one of items 1 to 35 having a Young's modulus from 74 GPa to 90 GPa.

A thirty-seventh item relates to a glass composition according to one of items 1 to 36 having a Poisson's ratio of from 0.220 to 0.270.

A thirty-eighth item relates to a glass composition according to one of items 1 to 37 having density of from 2.530 to 2.900 g/cm^3 .

A thirty-ninth item relates to a glass composition according to one of items 1 to 38 having packing density of from 0.44 to 0.58.

A fortieth item relates to a glass composition according to one of items 1 to 39 having a glass transition temperature T_g from 550°C to 700°C.

A forty-first item relates to a glass composition according to one of items 1 to 40 having a strain point of at least from 550°C to 670°C.

A forty-second item relates to a glass composition according to one of items 1 to 41 exhibiting one or more of

- a temperature T_4 of at least 960°C, at least 970°C, at least 1005°C, at least 1010°C, at least 1050°C or at least 1070°C,
- a temperature T_3 of at least 1180°C, at least 1200°C, at least 1225°C, at least 1250°C, at least 1310°C or at least 1330°C,
- a VFT constant A of <0.00 , optionally from -5.00 to -2.00,
- a VFT constant B of $>5,000^\circ\text{C}$, optionally from 5,800°C to 8,000°C, and
- a VFT constant T_0 of 140 to 450°C, such as from 145 to 300°C, or up to 255°C.

A forty-third item relates to a glass composition according to one of items 1 to 42, the glass having a steepness of its temperature-viscosity curve characterized by a difference between its temperatures T_4 and $T_{7.6}$ of from 200 to 400 K.

A forty-fourth item relates to a glass composition according to one of items 1 to 43, the glass having a steepness of its temperature-viscosity curve characterized by a difference between its temperatures T_4 and $T_{7.6}$ of from 250 to 380 K.

A forty-fifth item relates to a glass composition according to one of items 1 to 44 having a $CSS_{200\mu m}$ from 800 MPa to 1700 MPa.

A forty-sixth item relates to a glass composition according to one of items 1 to 45 having a $CSS_{30\mu m}$ from 600 MPa to 1200 MPa.

A forty-seventh item relates to a glass composition according to one of items 1 to 46 having a diffusivity from 10 to 80 $\mu m^2/h$.

A forty-eighth item relates to a glass composition according to one of items 1 to 47 having a chemical resistance characterized by one or more of

- (a) a hydrolytic resistance value in $\mu g/g$ sodium equivalent of less 320, or of less than 300, or of less than 280, or of less than 250, or of less than 225, or of less than 210;
- (b) an alkali resistance value in mg/dm^2 weight loss of less than 25, or of less than 22, or of less than 20, or of less than 18;
- (c) an acid resistance value in mg/dm^2 weight loss of less than 5.0, or of less than 2.5, or of less than 1.0.

A forty-ninth item relates to a glass composition according to one of items 1 to 48 having compressive stress susceptibility in MPa relative to the total content of alkali metal oxides R_2O and alkali earth metal oxides $R'O$ in weight percent $\frac{CSS_{200\mu m}}{[R_2O] + [R'O]}$ from 25 to 100.

A fiftieth item relates to a glass composition according to one of items 1 to 49 having a $CSS_{200\mu m}$ in MPa relative to the coefficient of thermal expansion in a temperature range of from 20 to 300°C in $ppm/K \frac{CSS_{200\mu m}}{CTE}$ from 100 to 250.

A fifty-first item relates to a glass composition according to one of items 1 to 50 having a refractive index n_d from 1.520 to 1.600.

A fifty-second item relates to a glass composition according to one of items 1 to 51 having no devitrification at all at the working point of 10^4 dPa*s.

A fifty-third item relates to a glass composition according to one of items 1 to 52 having a crystal growth rate at a viscosity of 10^5 dPa*s of at most 0.5 $\mu\text{m}/\text{min}$.

A fifty-fourth item relates to a glass comprising:

SiO ₂	46.0 to 65.0
Al ₂ O ₃	0.0 to 3.0
Na ₂ O	15.0 to 19.0
ZrO ₂	12.0 to 30.0

A fifty-fifth item relates to a glass composition according to item 54, having a CTE from 8.0 ppm/K to 9.0 ppm/K; or about 8.8 ppm/K.

A fifty-sixth item relates to a glass composition according to item 54, or item 55, having a Young's modulus from 70 GPa to 85 GPa, or about 78 GPa.

A fifty-seventh item relates to a glass composition according to item 54, or one of items 55 to 56, having a Poisson constant from 0.245 to 0.255, or about 0.250.

A fifty-eighth item relates to a glass composition according to item 54, or one of items 55 to 57, having a T_g from 600°C to 625°C, or about 611°C.

A fifty-ninth item relates to a glass composition according to item 54, or one of items 55 to 58, having a density from 2.600 g/cm³ to 2.725 g/cm³, or about 2.644 g/cm³.

A sixtieth item relates to a glass composition according to item 54, or one of items 55 to 59, having a packing density from 0.440 to 0.580, or from 0.50 to 0.54.

A sixty-first item relates to a glass composition according to item 54, or one of items 55 to 60, having a VFT A from -3.200 to -3.450, or about -3.375.

A sixty-second item relates to a glass composition according to item 54, or one of items 55 to 61, having a VFT B from 6700°C to 6850°C, or about 6776°C.

A sixty-third item relates to a glass composition according to item 54, or one of items 55 to 62, having a VFT T_0 from 200°C to 250°C, or about 213°C.

A sixty-fourth item relates to a glass composition according to item 54, or one of items 55 to 63, having a $T_{14.5}$ from 580°C to 600°C, or about 593°C.

A sixty-fifth item relates to a glass composition according to item 54, or one of items 55 to 64, having a T_{13} from 615°C to 640°C, or about 627°C.

A sixty-sixth item relates to a glass composition according to item 54, or one of items 55 to 65, having a $T_{7.6}$ from 815°C to 845°C, or about 831°C.

A sixty-seventh item relates to a glass composition according to item 54, or one of items 55 to 66, having a T_4 from 1100°C to 1200°C, or about 1132°C.

A sixty-eighth item relates to a glass composition according to item 54, or one of items 55 to 67, having a T_3 from 1200°C to 1300°C, or about 1276°C.

A sixty-ninth item relates to a glass composition according to item 54, or one of items 55 to 68, having a T_2 from 1400°C to 1500°C, or about 1474°C.

A seventieth item relates to a glass composition according to one of items 54 to 69 having a $CSS_{200\mu m}$ from 800 MPa to 1700 MPa.

A seventy-first item relates to a glass composition according to one of items 54 to 70 having a $CSS_{30\mu m}$ from 600 MPa to 1200 MPa.

A seventy-second item relates to a glass composition according to one of items 54 to 71 having a diffusivity from 10 to 80 $\mu m^2/h$.

A seventy-third item relates to a glass composition according to one of items 54 to 72 having a chemical resistance characterized by one or more of

- (a) a hydrolytic resistance value in $\mu g/g$ sodium equivalent of less than 210;
- (b) an alkali resistance value in mg/dm^2 weight loss of less than 18;
- (c) an acid resistance value in mg/dm^2 weight loss of less than 2.5, or of less than 1.0.

A seventy-fourth item relates to a glass composition according to one of items 54 to 73 having compressive stress susceptibility in MPa relative to the total content of alkali metal oxides R_2O and alkali earth metal oxides $R'O$ in weight percent $\frac{CSS_{200\mu m}}{[R_2O]+[R'O]}$ from 25 to 100.

A seventy-fifth item relates to a glass composition according to one of items 54 to 74 having a $CSS_{200\mu m}$ in MPa relative to the coefficient of thermal expansion in a temperature range of from 20 to 300°C in $\text{ppm/K} \frac{CSS_{200\mu m}}{CTE}$ from 100 to 250.

A seventy-sixth item relates to a glass article comprising the glass composition according to one of items 1 to 75, having a thickness of less than 1000 μm , less than 100 μm , less than 80 μm , or less than 60 μm , or less than 40 μm .

A seventy-seventh item relates to a glass article, optionally comprising the glass composition according to one of items 1 to 75, the article having less than 1000 μm thickness, wherein the article comprises a glass comprising SiO_2 in an amount of at least 40.0% by weight, Na_2O in an amount of at least 12.0% by weight, further comprising ZrO_2 , wherein the ratio of the amount by weight of ZrO_2 to the sum of amounts by weight of Al_2O_3 and B_2O_3 is at least 1.5, the glass having a $CSS_{30\mu m}$ of at least 700 MPa, and/or having an acid resistance of less than 5.0 mg/dm^2 or of less than 2.5 mg/dm^2 .

A seventy-eighth item relates to a glass article according to item 76 or 77, comprising an ion exchanged layer on one or both of its major surfaces, comprising a compressive stress of at least 400 MPa, at least 700 MPa, or at least 800 MPa.

A seventy-ninth item relates to a glass article according to one of items 76 to 78, having on one or both of its major surfaces, a ratio of compressive stress in MPa to article thickness in μm of at least 4.0 MPa/ μm , at least 5.0 MPa/ μm , or at least 10.0 MPa/ μm , or at least 20.0 MPa/ μm .

An eightieth item relates to a glass article according to one of items 76 to 79, a ratio of compressive stress in MPa to depth of ion exchanged layer in μm of at least 50 MPa/ μm , at least 75 MPa/ μm , or at least 90 MPa/ μm .

An eighty-first item relates to a glass article according to one of items 76 to 80, having a thickness of 1000 μm or less.

An eighty-second item relates to a glass article according to one of items 76 to 81, having a warp of less than 3.0 mm.

An eighty-third item relates to a glass article according to one of items 76 to 82, having a total thickness variation of less than 15.0 μm .

An eighty-fourth item relates to a glass article according to one of items 76 to 83, having a surface roughness R_a of not more than 5.0 nm.

An eighty-fifth item relates to a glass article according to one of items 76 to 84, having a remarkable chemical resistance characterized as one or more of

- (a) a hydrolytic resistance value in $\mu\text{g/g}$ sodium equivalent of less than 320, or of less than 300, or of less than 280, or of less than 250, or of less than 225, or of less than 210;
- (b) an alkali resistance value in mg/dm^2 weight loss of less than 25, or of less than 22, or of less than 20, or of less than 18;
- (c) an acid resistance value in mg/dm^2 weight loss of less than 5.0, or of less than 2.5, or of less than 1.0.

An eighty-sixth item relates to a glass article according to one of items 76 to 85, having a Vickers hardness of at least 580.

An eighty-seventh item relates to a glass article according to one of items 76 to 86, having three-point bending strength from 300 MPa to 400 MPa.

An eighty-eighth item relates to a glass article according to one of items 76 to 87, having compressive stress of at least 400 MPa.

An eighty-ninth item relates to a glass article according to one of items 76 to 88, having a thickness of 20 to 40 μm .

A ninetieth item relates to a glass article according to one of items 76 to 89, having a DoL on one or both of its major surfaces of from 6 to 11 μm .

A ninety-first item relates to a glass article according to one of items 76 to 90, having a DoL from 15 to 25% of the article thickness.

A ninety-second item relates to a glass article according to one of items 76 to 91, having a ratio of compressive stress in MPa to article thickness in μm of at least 4.0 MPa/ μm .

A ninety-third item relates to a glass article according to one of items 76 to 92, having on one or both of its major surfaces a ratio of compressive stress in MPa to depth of ion exchanged layer in μm of at least 50.

A ninety-fourth item relates to a glass article according to one of items 76 to 93, having a three-point bending strength of at least 400 MPa.

A ninety-fifth item relates to an electronic device comprising a glass composition according to one of items 1 to 75, and/or the glass article according to one of items 76 to 94.

Examples

Exemplary compositions of glasses according to this invention were prepared by melting appropriate glass raw materials. The following table provides an overview of compositions and properties of these glasses. Please note that the values in the tables have been rounded to one decimal place. Small rounding errors may therefore have occurred in the derivations and sums of the values.

1. Compositions examined

Table 1

Example No. [wt. %]	1	2	3	4	5	6
SiO ₂	61.5	63.7	64.7	63.2	61.0	60.6
Al ₂ O ₃	0.2	0.2	2.5	2.3	0.9	0.1
B ₂ O ₃	2.3	< 100 ppm	< 100 ppm	< 100 ppm	< 100 ppm	< 100 ppm
P ₂ O ₅	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	3.4
Fe ₂ O ₃	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Na ₂ O	17.2	17.3	16.8	18.0	17.0	17.0
K ₂ O	< 100 ppm	< 100 ppm	< 100 ppm	0.6	0.7	0.0
MgO	5.0	5.1	2.5	0.0	4.4	5.0
CaO	< 150 ppm	< 150 ppm	< 150 ppm	2.0	< 150 ppm	< 150 ppm
ZrO ₂	13.0	13.0	12.7	13.2	15.2	13.2
TiO ₂	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
SnO ₂	0.1	0.1	0.1	0.1	0.1	0.1
Cl	0.3	0.3	0.2	0.3	0.3	0.3
HfO ₂	0.3	0.3	0.3	0.3	0.3	0.3
Properties						
CTE [ppm/K]	8.65	8.65	8.31	9.00	8.80	8.68
Young's modulus [GPa]	80	78	77	77	80	77
Poisson constant	0.251	0.250	0.243	0.249	0.247	0.247
T _g [°C]	601	611	613	594	628	609
Density [g/cm ³]	2.6567	2.6444	2.6216	2.6530	2.6865	2.6464
Packing density	0.518	0.512	0.509	0.515	0.516	0.513
VFT A	-2.980	-3.375	-3.597	-3.286	-3.905	-3.534
VFT B [°C]	5876.7	6775.4	7687.3	6979.4	7443.1	7051.1
VFT T ₀ [°C]	243.7	213.6	170.6	180.3	206.7	196.3
T _{14.5} [°C]	580	593	595	573	611	587
T ₁₃ [°C]	611	627	634	609	647	623
T _{7.6} [°C]	799	831	857	821	854	830

Example No. [wt. %]	1	2	3	4	5	6
T ₄ [°C]	1086	1132	1182	1138	1148	1132
T ₃ [°C]	1226	1276	1336	1291	1285	1275
T ₂ [°C]	1424	1474	1544	1501	1467	1470

Table 2

Example No. [wt. %]	7	8	9	10	11	12
SiO ₂	59.8	56.7	58.0	61.7	60.2	63.6
Al ₂ O ₃	0.1	0.8	0.1	0.1	0.1	0.1
B ₂ O ₃	< 100 ppm	< 100 ppm	< 100 ppm	< 100 ppm	< 100 ppm	< 100 ppm
P ₂ O ₅	< 0.1	< 0.1	0.1	< 0.1	< 0.1	< 0.1
Fe ₂ O ₃	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
TiO ₂	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Na ₂ O	16.8	18.1	17.3	16.9	17.5	15.5
K ₂ O	2.8	1.9	0.7	< 100 ppm	< 100 ppm	< 100 ppm
MgO	3.7	1.5	2.8	< 100 ppm	7.7	6.4
CaO	< 150 ppm	1.0	1.5	7.2	< 150 ppm	< 150 ppm
ZrO ₂	16.0	17.4	20.2	13.2	13.8	13.7
ZnO	< 100 ppm	1.8	< 100 ppm	< 100 ppm	< 100 ppm	< 100 ppm
SnO ₂	0.1	0.1	0.1	0.1	0.1	0.1
Cl	0.2	0.3	0.2	0.3	0.3	0.3
HfO ₂	0.3	0.3	0.4	0.3	0.3	0.3
Properties						
CTE [ppm/K]	9.36	9.57	8.70	9.12	8.89	8.05
Young's modulus [GPa]	81	82	84	82	81	82
Poisson constant	0.253	0.258	0.254	0.251	0.252	0.248
T _g [°C]	610	611	670	613	622	637
Density [g/cm ³]	2.7030	2.7759	2.7732	2.7099	2.6899	2.6600
Packing density	0.522	0.525	0.521	0.521	0.517	0.512
VFT A	-4.137	-4.180	-4.566	-2.844	-3.219	-3.259
VFT B [°C]	7877.8	7604.1	8072.0	5537.0	5943.0	6431.7
VFT T ₀ [°C]	168.9	189.0	234.3	279.0	270.6	261.0
T _{14.5} [°C]	592	596	658	598	606	623
T ₁₃ [°C]	629	632	694	628	637	657
T _{7.6} [°C]	840	835	898	809	820	853
T ₄ [°C]	1137	1119	1177	1088	1094	1147
T ₃ [°C]	1273	1248	1301	1226	1226	1289

Example No. [wt. %]	7	8	9	10	11	12
T ₂ [°C]	1453	1419	1464	1422	1409	1484

Table 3

Example No. [wt. %]	13	14	15
SiO ₂	58.9	63.9	62.7
Al ₂ O ₃	3.0	0.1	1.2
Li ₂ O	< 100 ppm	0.9	< 100 ppm
B ₂ O ₃	< 100 ppm	< 100 ppm	< 100 ppm
P ₂ O ₅	< 0.1	< 0.1	< 0.1
Fe ₂ O ₃	< 0.1	< 0.1	< 0.1
TiO ₂	< 0.1	< 0.1	< 0.1
Na ₂ O	16.2	15.6	17.3
K ₂ O	1.4	< 100 ppm	< 100 ppm
MgO	5.6	5.1	5.0
CaO	< 150 ppm	< 150 ppm	< 150 ppm
ZrO ₂	14.4	13.6	13.3
SnO ₂	< 100 ppm	< 100 ppm	< 100 ppm
SO ₃	0.2	< 100 ppm	0.1
Cl	< 0.1	0.3	< 0.1
HfO ₂	0.3	0.3	0.3
Properties			
CTE [ppm/K]	8.82	8.64	8.65
Young's modulus [GPa]	83	83	79
Poisson constant	0.248	0.249	0.245
T _g [°C]	641	567	620
Density [g/cm ³]	2.6869	2.6557	2.6521
Packing density	n.d.	0.514	n.d.
VFT A	-3.350	-3.724	-3.376
VFT B [°C]	6367.4	7430.8	6706.2
VFT T ₀ [°C]	270.5	145.4	230.9
T _{14.5} [°C]	627	553	606
T ₁₃ [°C]	660	590	640
T _{7.6} [°C]	852	802	842
T ₄ [°C]	1137	1107	1140
T ₃ [°C]	1273	1251	1283
T ₂ [°C]	1461	1444	1478

The packing density was determined by dividing the ionic volume by the molar volume of the glass, wherein the ionic volume is the volume taken by one mol of the ions that make up the glass, and wherein the molar volume is the quotient of the molar weight and the measured density of the glass. For calculations of the volume of each type of ion, the effective ionic radii according to Shannon are employed with coordination numbers calculated using Pauling's rules.

2. Ion exchange treatment

Thin sheets of glass were prepared from compositions 1 to 7. The sheet thickness was 200 μm . Subsequently, the sheets were ion exchange treated in a 100% KNO_3 salt bath at 440 $^{\circ}\text{C}$ for 30 minutes. The resulting compressive stress and depth of the ion exchanged layer (DoL) are listed in the following table.

Table 4

Example No.	1	2	3	4	5	6	7
Compressive stress [MPa]	1077	1319	1143	1064	1331	1180	1201
DoL [μm]	6.3	7.7	9.1	11.2	8.3	9.6	11.1
R_2O [wt.%]	17.2	17.3	16.8	18.6	17.7	17.0	19.6
CTE [ppm/K]	8.65	8.65	8.31	9.00	8.80	8.68	9.36
$\frac{\text{CSS}_{200\mu\text{m}}}{[\text{R}_2\text{O}]+[\text{R}'\text{O}]}$ [MPa/wt%]	48.4	59.0	59.2	52.0	60.3	53.7	51.5
$\text{CSS}_{200\mu\text{m}}/\text{CTE}$ [MPa $\cdot\text{K}/\text{ppm}$]	124.5	152.5	137.5	118.2	151.3	135.9	128.3
CS/article thickness [MPa/ μm]	5.4	6.6	5.7	5.3	6.7	5.9	6.0
CS/DoL [MPa/ μm]	171	171	126	95	160	123	108
D [$\mu\text{m}^2/\text{h}$]	10.1	15.1	21.1	32.0	17.6	23.5	31.4

3. Chemical resistance

Chemical resistance was tested for glass No. 2. Hydrolytic resistance was tested according to ISO 719. Alkali resistance was measured according to ISO 695, and acid resistance was tested in accordance with DIN 12116. The results are:

- hydrolytic resistance [$\mu\text{g}/\text{g}$]: 172,
- alkali resistance [mg/dm^2]: 15,
- acid resistance [mg/dm^2]: 0.7.

4. Devitrification

The devitrification resistance was determined in terms of crystal growth rate (in $\mu\text{m}/\text{min}$) at a viscosity of 10^5 dPa*s for compositions 1, 2, 3 and 7. The lower the crystal growth rate is, the higher is the devitrification resistance. The measurement of the crystal growth rate is well known. The crystal growth rate is measured along the formed crystals, i.e., at their greatest extension.

Briefly, the crystal growth rate was determined by thermally treating the glass for 16 hours in a gradient furnace with increasing temperature regimen. Importantly, if no devitrification occurs at all at a viscosity of 10^5 dPa*s, a crystal growth rate at 10^5 dPa*s cannot be determined. No devitrification may also be expressed as a crystal growth rate of 0 $\mu\text{m}/\text{min}$ at 10^5 dPa*s.

The crystallization rate was determined using glass grains of ca. 2 mm to 3 mm diameter. The glass grains were put onto a platinum carrier for the gradient tempering. The carrier had depressions, each for taking up a glass grain, and a hole at the bottom of each depression for optical inspection so that the crystal growth rate was determined microscopically. The depressions had a diameter of 2 mm each and the holes had a diameter of 0.9 mm each.

The results are shown in the following table.

Example No.	Crystal growth rate at 10^5 dPa*s (in $\mu\text{m}/\text{min}$)
1	0
2	0 to 0.03
3	0
7	0.07 to 0.08

Claims

1. A glass comprising the following components:
 - i. SiO_2 ,
 - ii. Al_2O_3 in an amount of 0.0 to 6.0% by weight,
 - ii. ZrO_2 in an amount of at least 8.0% by weight,
 - iii. Na_2O in an amount of at least 12.0% by weight,
 - iv. 0.0 to 5.0% by weight of B_2O_3
 - v. 0.0 to 5.0% by weight of Li_2O ,
 - vi. 0.0 to 10.0% by weight of K_2O ; and
 - vii. optionally, one or more components selected from P_2O_5 and TiO_2 .
2. A glass according to claim 1, comprising the following components in percent by weight:

SiO_2	40.0 to 70.0
Al_2O_3	0.0 to 6.0
Na_2O	12.0 to 25.0
ZrO_2	8.0 to 32.0
B_2O_3	0.0 to 5.0
Li_2O	0.0 to 5.0
K_2O	0.0 to 10.0
MgO	0.0 to 20.0
CaO	0.0 to 15.0
$\text{MgO}+\text{CaO}$	at least 1.5
SrO	0.0 to 10.0
BaO	0.0 to 10.0
ZnO	0.0 to 10.0
P_2O_5	0.0 to 10.0
TiO_2	0.0 to 5.0
Y_2O_3	0.0 to 20.0
La_2O_3	0.0 to 10.0
Nb_2O_5	0.0 to 10.0

Cl	0.0 to 1.0
HfO ₂	0.0 to 1.0

and, optionally, comprising dyes or colorants, such as Fe₂O₃, CoO, and/or Cr₂O₃.

3. Glass according to one of the preceding claims, being free of As₂O₃ and/or Sb₂O₃.
4. Glass according to one of the preceding claims, having a coefficient of thermal expansion in a temperature range of from 20 to 300°C of less than $15.0 \cdot 10^{-6} \text{ K}^{-1}$, less than $12.0 \cdot 10^{-6} \text{ K}^{-1}$, less than $10.0 \cdot 10^{-6} \text{ K}^{-1}$, less than $9.8 \cdot 10^{-6} \text{ K}^{-1}$.
5. Glass according to one of the preceding claims, having a compressive stress susceptibility defined as a CSS_{30μm} score of at least 700 MPa.
6. Glass according to one of the preceding claims, wherein the amount of ZrO₂ is >10.0% by weight.
7. Glass according to one of the preceding claims, wherein a ratio of the amount of ZrO₂ to the amount of Al₂O₃ in percent by weight is at least 1.5, or at least 2.0.
8. Glass according to one of the preceding claims, having a 1000 MPa IOX-time of less than 60 minutes.
9. Glass according to one or more of the preceding claims, having a glass transition temperature T_g of at least 540°C, at least 550°C or at least 560°C.
10. Glass according to one or more of the preceding claims, the glass having a steepness of its temperature-viscosity curve characterized by a difference between its temperatures T₄ and T_{7.6} of from 250 to 350 K.
11. Glass according to one or more of the preceding claims, wherein the glass has a diffusivity of at least 8 μm²/h, or at least 10 μm²/h.
12. Glass according to one or more of the preceding claims, wherein the acid resistance value in mg/dm² weight loss is less than 5.0.
13. Glass according to one or more of the preceding claims, wherein the crystal growth rate is at most 0.5 μm/min at a viscosity of 10⁵ dPa*s, when the glass is thermally treated for 16 hours in a gradient furnace with increasing temperature regimen.

14. Glass according to one or more of the preceding claims, wherein the Young's modulus is between 70 and 90 GPa.
15. A glass article, optionally a glass according to one of claims 1 to 15, having less than 1000 μm thickness, wherein the article comprises a glass comprising SiO_2 in an amount of at least 40.0% by weight, Na_2O in an amount of at least 12.0% by weight, further comprising ZrO_2 , wherein the ratio of the amount by weight of ZrO_2 to the sum of the amounts by weight of Al_2O_3 and B_2O_3 is at least 1.5, the glass having a $\text{CSS}_{30\mu\text{m}}$ of at least 700 MPa and/or having an acid resistance of less than 5.0 mg/dm^2 , or an acid resistance of less than 2.5 mg/dm^2 .
16. Glass article according to claim 15, having a thickness of less than 100 μm , less than 80 μm , less than 60 μm , or less than 40 μm .
17. Glass article according to at least one of claims 15 to 16 comprising an ion exchanged layer on one or both of its major surfaces.
18. Glass article according to claim 17, having on the one or both of its major surfaces, a compressive stress of at least 400 MPa, at least 700 MPa, or at least 800 MPa.
19. Glass article according to claim 17 or 18, having on the one or both of its major surfaces, a ratio of compressive stress in MPa to article thickness in μm of at least 4.0 MPa/ μm , at least 5.0 MPa/ μm , at least 10.0 MPa/ μm , at least 15.0 MPa/ μm , or at least 20.0 MPa/ μm .
20. Glass article according to at least one of claims 17 to 19, having, on the one or both of its major surfaces, a ratio of compressive stress in MPa to depth of ion exchanged layer in μm of at least 50 MPa/ μm , at least 75 MPa/ μm , or at least 90 MPa/ μm .
21. An electronic device comprising a glass according to any one of claims 1 to 14, and/or a glass article according to one of claim 15 to 20.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2023/101637

A. CLASSIFICATION OF SUBJECT MATTER

C03C3/076(2006.01)i; C03C3/083(2006.01)i; C03C3/085(2006.01)i; C03C3/087(2006.01)i; C03C3/089(2006.01)i;
C03C3/093(2006.01)i; C03B27/03(2006.01)i

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)

C03B, C03C

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)

ENTXT, VEN, CNABS, CNTXT, CNKI, ISI: glass, silica, alumina, sodium oxide, zirconia, strengthen, harden, toughen, reinforce, tempered, enhance, ion exchange, SiO₂, Al₂O₃, Na₂O, ZrO₂

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 107531549 A (PILKINGTON GROUP CO LTD) 02 January 2018 (2018-01-02) claims 1-13	1-21
X	US 4212919 A (CORNING GLASS WORKS) 15 July 1980 (1980-07-15) claims 1-5	1-21
X	JP H09110453 A (NIPPON GLASS FIBER CO LTD) 28 April 1997 (1997-04-28) claims 1-5	1-21
X	SU 441244 A1 (GLASS RES INST) 30 August 1974 (1974-08-30) claim 1	1-21
A	JP 2017088484 A (OHARA KK) 25 May 2017 (2017-05-25) the whole document	1-21
A	JP S5641859 A (TEIJIN LTD) 18 April 1981 (1981-04-18) the whole document	1-21



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
 “D” document cited by the applicant in the international application
 “E” earlier application or patent but published on or after the international filing date
 “L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
 “O” document referring to an oral disclosure, use, exhibition or other means
 “P” document published prior to the international filing date but later than the priority date claimed

“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

“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

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&” document member of the same patent family

Date of the actual completion of the international search

12 March 2024

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2023/101637

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				JP	6655629	B2	26 February 2020
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