



US 20130101764A1

(19) **United States**

(12) **Patent Application Publication**
Schaut et al.

(10) **Pub. No.: US 2013/0101764 A1**

(43) **Pub. Date: Apr. 25, 2013**

(54) **GLASS ARTICLES WITH IMPROVED
CHEMICAL AND MECHANICAL
DURABILITY**

Publication Classification

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(51) **Int. Cl.**
C03C 4/00 (2006.01)
C03C 3/083 (2006.01)
(52) **U.S. Cl.**
USPC **428/34.4; 428/410**

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(57) **ABSTRACT**

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A glass article may formed from a glass composition that may include from about 70 mol. % to about 78 mol. % SiO₂, from about 3 mol. % to about 13 mol. % alkaline earth oxide, X mol. % Al₂O₃, and Y mol. % alkali oxide. The alkali oxide may include Na₂O in an amount greater than or equal to about 9 mol. % and less than or equal to about 15 mol. %. The ratio of Y:X may be greater than 1. The glass article may be free of boron and compounds of boron. The glass article may have a compressive stress layer with a compressive stress greater than or equal to about 250 MPa and depth of layer greater than or equal to about 25 μm. The glass article may have at least a type HGA2 hydrolytic resistance according to the ISO 720 standard.

(21) Appl. No.: **13/660,683**

(22) Filed: **Oct. 25, 2012**

Related U.S. Application Data

(60) Provisional application No. 61/551,163, filed on Oct. 25, 2011.

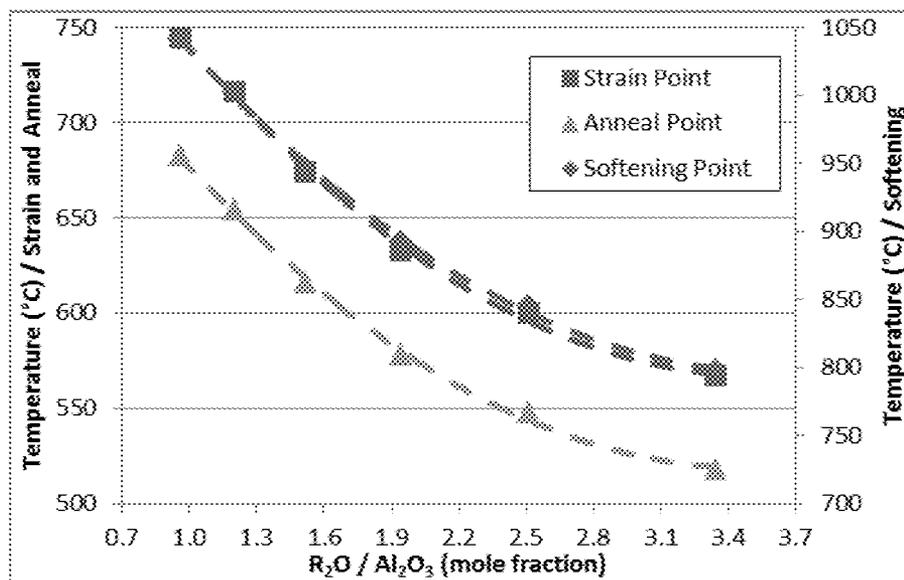


FIG. 1

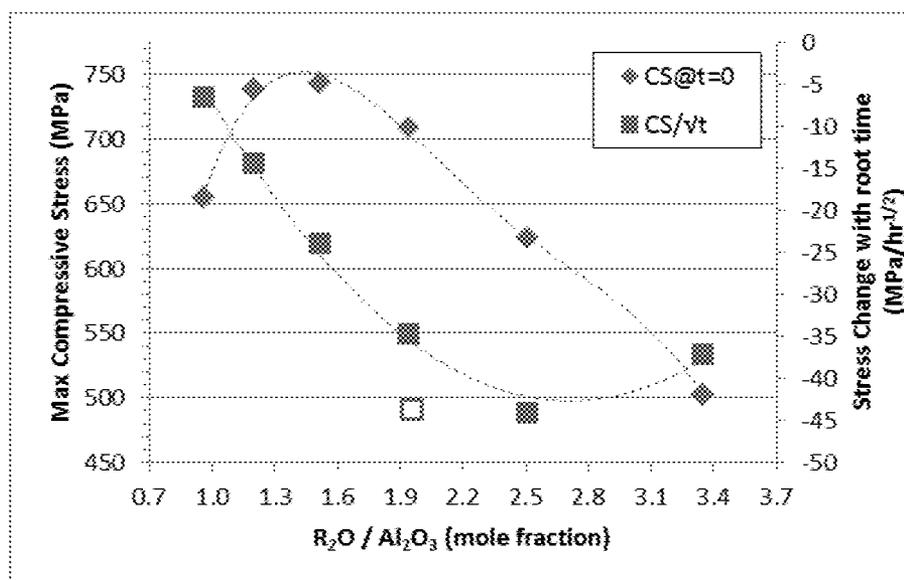


FIG. 2

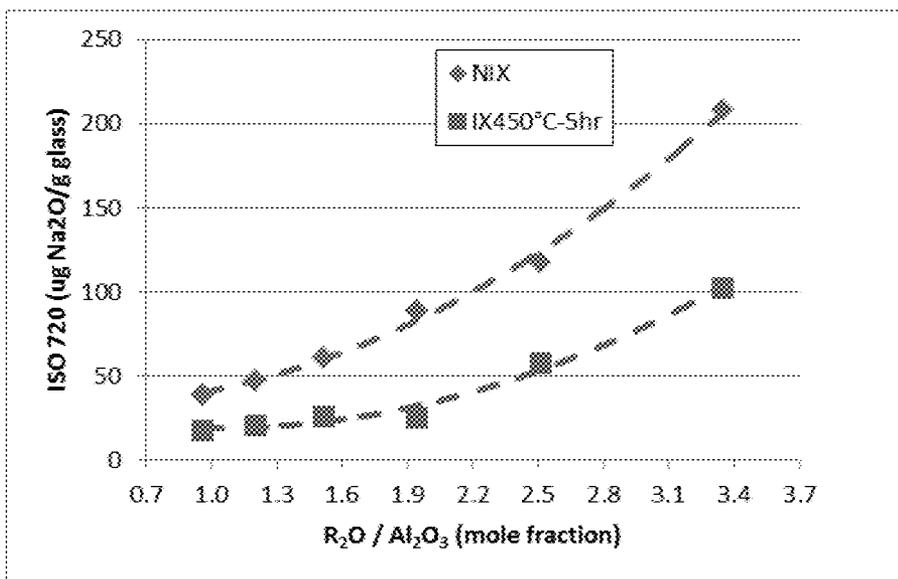


FIG. 3

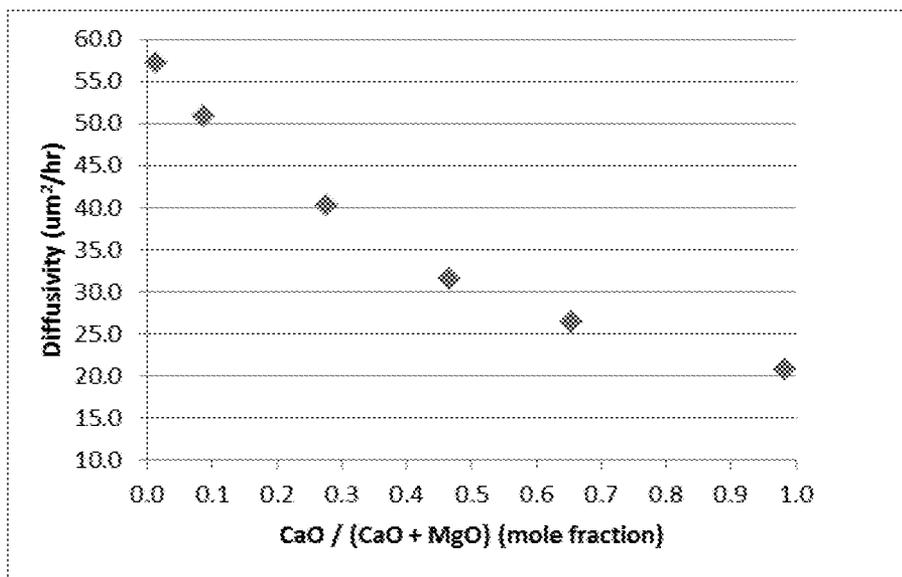


FIG. 4

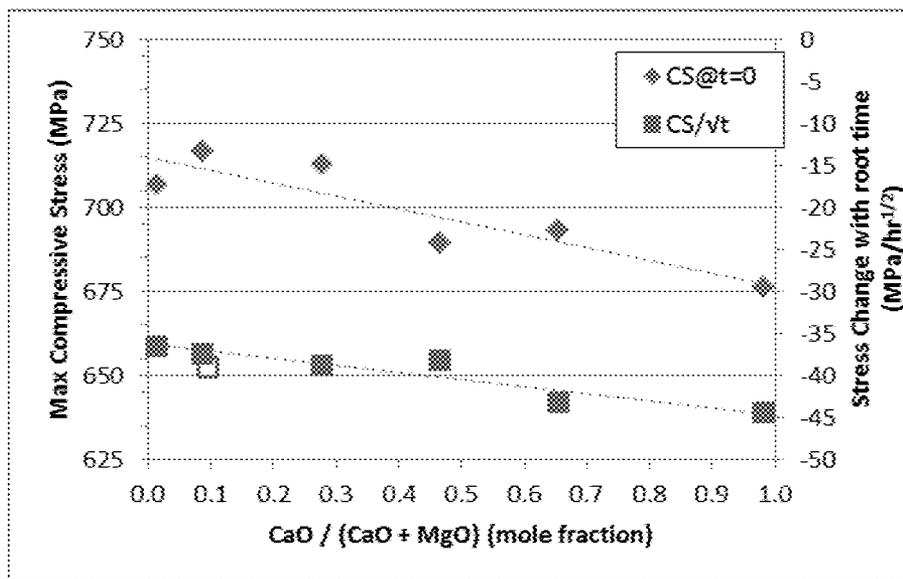


FIG. 5

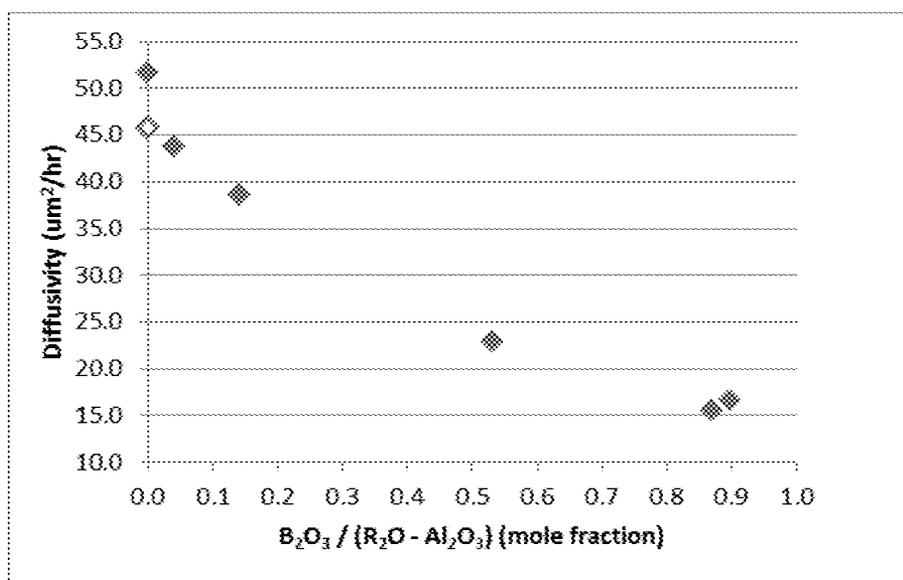


FIG. 6

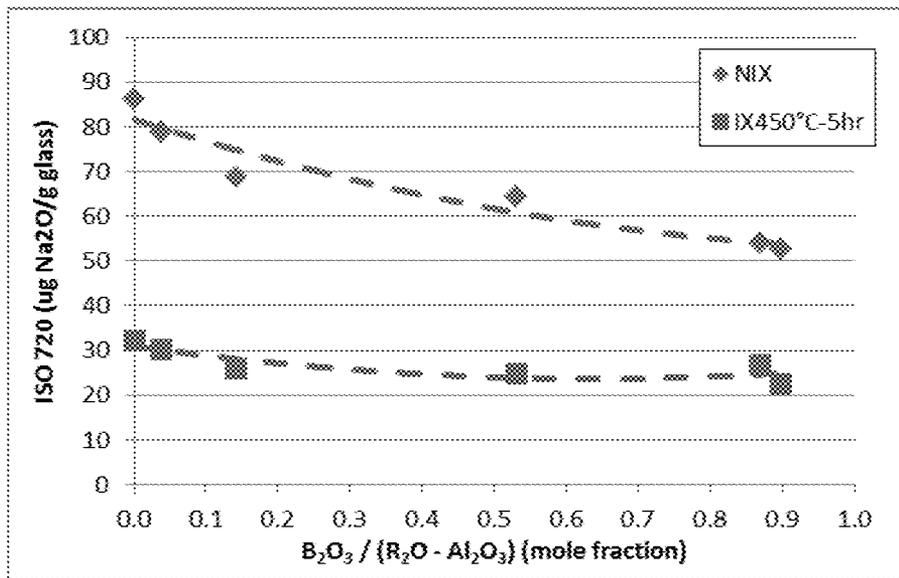


FIG. 7

GLASS ARTICLES WITH IMPROVED CHEMICAL AND MECHANICAL DURABILITY

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims priority to U.S. Provisional Patent Application Ser. No. 61/551,163, filed Oct. 25, 2011 (Attorney Docket No. SP11-240P) and entitled "Glass Compositions With Improved Chemical and Mechanical Durability," the entirety of which is incorporated by reference herein.

BACKGROUND

Field

[0002] The present specification generally relates to glass articles and, more specifically, to chemically and mechanically durable glass articles.

Technical Background

[0003] Historically, glass has been used as a preferred material for many applications, including food and beverage packaging, kitchen and laboratory glassware, and windows or other architectural features, because of its hermeticity, optical clarity and excellent chemical durability relative to other materials. For various applications, glass articles must have acceptable chemical durability, which often depends on the context in which the glass article is used. For example, the glass used in beverage packaging applications must have adequate chemical durability so as not to contaminate the beverage contained therein.

[0004] However, use of glass for many applications is limited by the mechanical performance of the glass. A strong glass is desirable in many applications, such as windshield or windows. Additionally, in the food and beverage packaging industry, glass breakage is a safety concern for the end user as the broken package and/or the contents of the package may injure the end user. Breakage can be costly to many food or beverage packaging industries because, for example, breakage within a filling line may require that neighboring unbroken containers be discarded as the containers may contain fragments from the broken container. Breakage may also require that the filling line be slowed or stopped, lowering production yields. Further, non-catastrophic breakage (i.e., when the glass cracks but does not break) may cause the contents to lose their sterility which, in turn, may result in costly product recalls.

[0005] One approach to improving the mechanical durability of the glass article is to thermally temper the glass article. Thermal tempering strengthens glass by inducing a surface compressive stress during rapid cooling after forming. This technique works well for glass articles with flat geometries (such as windows), glass articles with thicknesses >2 mm, and glass compositions with high thermal expansion. However, for many glass article applications it is desirable or required to have complex geometries, thin walls (~1-1.5 mm), and are produced from low expansion glasses ($30\text{-}55 \times 10^{-7} \text{K}^{-1}$) making many glass articles unsuitable for strengthening by thermal tempering.

[0006] Chemical tempering also strengthens glass by the introduction of surface compressive stress. The stress is introduced by submerging the article in a molten salt bath. As ions

from the glass are replaced by larger ions from the molten salt, a compressive stress is induced in the surface of the glass. The advantage of chemical tempering is that it can be used on complex geometries, thin samples, and is relatively insensitive to the thermal expansion characteristics of the glass substrate. However, glass compositions which exhibit a moderate susceptibility to chemical tempering generally exhibit poor chemical durability and vice-versa.

[0007] Accordingly, a need exists for glass articles formed from glass compositions which are chemically durable and susceptible to chemical strengthening by ion exchange.

SUMMARY

[0008] According to one embodiment, a glass article may be formed from a glass composition comprising from about 70 mol. % to about 78 mol. % SiO_2 , from about 3 mol. % to about 13 mol. % alkaline earth oxide, X mol. % Al_2O_3 , and Y mol. % alkali oxide. The alkali oxide may comprise Na_2O in an amount greater than or equal to about 9 mol. % and less than or equal to about 15 mol. %. The ratio of Y:X may be greater than 1. The glass article may be free of boron and compounds of boron. The glass article may comprise a compressive stress layer with a compressive stress greater than or equal to about 250 MPa and depth of layer greater than or equal to about 25 μm . The glass article may have at least a type HGA2 hydrolytic resistance according to ISO 720.

[0009] According to another embodiment, a glass article may be formed from a glass composition comprising from about 70 mol. % to about 78 mol. % SiO_2 , from about 3 mol. % to about 13 mol. % alkaline earth oxide, X mol. % Al_2O_3 , and Y mol. % alkali oxide. The alkaline earth oxide may comprise from about 0.1 mol. % to about 1.0 mol. % CaO . The alkali oxide may comprise Na_2O in an amount greater than or equal to about 9 mol. % and less than or equal to about 15 mol. %. A ratio of Y:X may be from about 1 to about 2. The glass article may be free of boron and compounds of boron. The glass article may comprise a compressive stress layer with a compressive stress greater than or equal to about 250 MPa and depth of layer greater than or equal to about 25 μm . The glass article may have at least a type HGA2 hydrolytic resistance according to ISO 720. The glass article may be a beverage package, a food package, household glassware, laboratory glassware, a cosmetics package, structural glazing, automobile glazing, cookware, a lighting product, an ornamental item, display glass, industrial tubing, or a scientific instrument.

[0010] Additional features and advantages will be set forth in the detailed description which follows, and in part will be readily apparent to those skilled in the art from that description or recognized by practicing the embodiments described herein, including the detailed description which follows, the claims, as well as the appended drawings.

[0011] It is to be understood that both the foregoing general description and the following detailed description describe various embodiments and are intended to provide an overview or framework for understanding the nature and character of the claimed subject matter. The accompanying drawings are included to provide a further understanding of the various embodiments, and are incorporated into and constitute a part of this specification. The drawings illustrate the various embodiments described herein, and together with the description serve to explain the principles and operations of the claimed subject matter.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] FIG. 1 graphically depicts the relationship between the ratio of alkali oxides to alumina (x-axis) and the strain point, annealing point, and softening point (y-axes) of inventive and comparative glass compositions;

[0013] FIG. 2 graphically depicts the relationship between the ratio of alkali oxides to alumina (x-axis) and the maximum compressive stress and stress change (y-axes) of inventive and comparative glass compositions;

[0014] FIG. 3 graphically depicts the relationship between the ratio of alkali oxides to alumina (x-axis) and hydrolytic resistance as determined from the ISO 720 standard (y-axis) of inventive and comparative glass compositions;

[0015] FIG. 4 graphically depicts diffusivity D (y-axis) as a function of the ratio $(\text{CaO}/(\text{CaO}+\text{MgO}))$ (x-axis) for inventive and comparative glass compositions;

[0016] FIG. 5 graphically depicts the maximum compressive stress (y-axis) as a function of the ratio $(\text{CaO}/(\text{CaO}+\text{MgO}))$ (x-axis) for inventive and comparative glass compositions;

[0017] FIG. 6 graphically depicts diffusivity D (y-axis) as a function of the ratio $(\text{B}_2\text{O}_3/(\text{R}_2\text{O}-\text{Al}_2\text{O}_3))$ (x-axis) for inventive and comparative glass compositions; and

[0018] FIG. 7 graphically depicts the hydrolytic resistance as determined from the ISO 720 standard (y-axis) as a function of the ratio $(\text{B}_2\text{O}_3/(\text{R}_2\text{O}-\text{Al}_2\text{O}_3))$ (x-axis) for inventive and comparative glass compositions.

DETAILED DESCRIPTION

[0019] Reference will now be made in detail to various embodiments of glass articles comprising glass compositions which exhibit improved chemical and mechanical durability. Such glass compositions are suitable for use in a wide variety of applications. The glass compositions may also be chemically strengthened thereby imparting increased mechanical durability to the glass. The glass compositions described herein generally comprise silica (SiO_2), alumina (Al_2O_3), alkaline earth oxides (such as MgO and/or CaO), and alkali oxides (such as Na_2O and/or K_2O) in amounts which impart chemical durability to the glass composition. Moreover, the alkali oxides present in the glass compositions facilitate chemically strengthening the glass compositions by ion exchange. Various embodiments of the glass compositions will be described herein and further illustrated with reference to specific examples.

[0020] The term “softening point,” as used herein, refers to the temperature at which the viscosity of the glass composition is $1 \times 10^{7.6}$ poise.

[0021] The term “annealing point,” as used herein, refers to the temperature at which the viscosity of the glass composition is 1×10^{13} poise.

[0022] The terms “strain point” and “ T_{strain} ” as used herein, refers to the temperature at which the viscosity of the glass composition is 3×10^{14} poise.

[0023] The term “CTE,” as used herein, refers to the coefficient of thermal expansion of the glass composition over a temperature range from about room temperature (RT) to about 300° C.

[0024] In the embodiments of the glass compositions described herein, the concentrations of constituent components (e.g., SiO_2 , Al_2O_3 , and the like) are specified in mole percent (mol. %) on an oxide basis, unless otherwise specified.

[0025] The terms “free” and “substantially free,” when used to describe the concentration and/or absence of a particular constituent component in a glass composition, means that the constituent component is not intentionally added to the glass composition. However, the glass composition may contain traces of the constituent component as a contaminant or tramp in amounts of less than 0.01 mol. %.

[0026] The term “chemical durability,” as used herein, refers to the ability of the glass composition to resist degradation upon exposure to specified chemical conditions. Specifically, the chemical durability of the glass compositions described herein was assessed according to three established material testing standards: DIN 12116 dated March 2001 and entitled “Testing of glass—Resistance to attack by a boiling aqueous solution of hydrochloric acid—Method of test and classification”; ISO 695:1991 entitled “Glass—Resistance to attack by a boiling aqueous solution of mixed alkali—Method of test and classification”; and ISO 720:1985 entitled “Glass—Hydrolytic resistance of glass grains at 121 degrees C.—Method of test and classification.” The chemical durability of the glass may also be assessed according to ISO 719:1985 “Glass—Hydrolytic resistance of glass grains at 98 degrees C.—Method of test and classification,” in addition to the above referenced standards. The ISO 719 standard is a less rigorous version of the ISO 720 standard and, as such, it is believed that a glass which meets a specified classification of the ISO 720 standard will also meet the corresponding classification of the ISO 719 standard. The classifications associated with each standard are described in further detail herein.

[0027] The glass compositions described herein are alkali aluminosilicate glass compositions which generally include a combination of SiO_2 , Al_2O_3 , at least one alkaline earth oxide, and one or more alkali oxides, such as Na_2O and/or K_2O . In some embodiments, the glass compositions may be free from boron and compounds containing boron. The combination of these components enables a glass composition which is resistant to chemical degradation and is also suitable for chemical strengthening by ion exchange. In some embodiments the glass compositions may further comprise minor amounts of one or more additional oxides such as, for example, SnO_2 , ZrO_2 , ZnO , TiO_2 , As_2O_3 or the like. These components may be added as fining agents and/or to further enhance the chemical durability of the glass composition.

[0028] In the embodiments of the glass compositions described herein SiO_2 is the largest constituent of the composition and, as such, is the primary constituent of the resulting glass network. SiO_2 enhances the chemical durability of the glass and, in particular, the resistance of the glass composition to decomposition in acid and the resistance of the glass composition to decomposition in water. Accordingly, a high SiO_2 concentration is generally desired. However, if the content of SiO_2 is too high, the formability of the glass may be diminished as higher concentrations of SiO_2 increase the difficulty of melting the glass which, in turn, adversely impacts the formability of the glass. In the embodiments described herein, the glass composition generally comprises SiO_2 in an amount greater than or equal to 67 mol. % and less than or equal to about 80 mol. % or even less than or equal to 78 mol. %. In some embodiments, the amount of SiO_2 in the glass composition may be greater than about 68 mol. %, greater than about 69 mol. % or even greater than about 70 mol. %. In some other embodiments, the amount of SiO_2 in the glass composition may be greater than 72 mol. %, greater than 73

mol. % or even greater than 74 mol. %. For example, in some embodiments, the glass composition may include from about 68 mol. % to about 80 mol. % or even to about 78 mol. % SiO_2 . In some other embodiments the glass composition may include from about 69 mol. % to about 80 mol. % or even to about 78 mol. % SiO_2 . In some other embodiments the glass composition may include from about 70 mol. % to about 80 mol. % or even to about 78 mol. % SiO_2 . In still other embodiments, the glass composition comprises SiO_2 in an amount greater than or equal to 70 mol. % and less than or equal to 78 mol. %. In some embodiments, SiO_2 may be present in the glass composition in an amount from about 72 mol. % to about 78 mol. %. In some other embodiments, SiO_2 may be present in the glass composition in an amount from about 73 mol. % to about 78 mol. %. In other embodiments, SiO_2 may be present in the glass composition in an amount from about 74 mol. % to about 78 mol. %. In still other embodiments, SiO_2 may be present in the glass composition in an amount from about 70 mol. % to about 76 mol. %.

[0029] The glass compositions described herein further include Al_2O_3 . Al_2O_3 , in conjunction with alkali oxides present in the glass compositions such as Na_2O or the like, improves the susceptibility of the glass to ion exchange strengthening. In the embodiments described herein, Al_2O_3 is present in the glass compositions in X mol. % while the alkali oxides are present in the glass composition in Y mol. %. The ratio Y:X in the glass compositions described herein is greater than 1 in order to facilitate the aforementioned susceptibility to ion exchange strengthening. Specifically, the diffusion coefficient or diffusivity D of the glass composition relates to the rate at which alkali ions penetrate into the glass surface during ion exchange. Glasses which have a ratio Y:X greater than about 0.9 or even greater than about 1 have a greater diffusivity than glasses which have a ratio Y:X less than 0.9. Glasses in which the alkali ions have a greater diffusivity can obtain a greater depth of layer for a given ion exchange time and ion exchange temperature than glasses in which the alkali ions have a lower diffusivity. Moreover, as the ratio of Y:X increases, the strain point, anneal point, and softening point of the glass decrease, such that the glass is more readily formable. In addition, for a given ion exchange time and ion exchange temperature, it has been found that compressive stresses induced in glasses which have a ratio Y:X greater than about 0.9 and less than or equal to 2 are generally greater than those generated in glasses in which the ratio Y:X is less than 0.9 or greater than 2. Accordingly, in some embodiments, the ratio of Y:X is greater than 0.9 or even greater than 1. In some embodiments, the ratio of Y:X is greater than 0.9, or even greater than 1, and less than or equal to about 2. In still other embodiments, the ratio of Y:X may be greater than or equal to about 1.3 and less than or equal to about 2.0 in order to maximize the amount of compressive stress induced in the glass for a specified ion exchange time and a specified ion exchange temperature.

[0030] However, if the amount of Al_2O_3 in the glass composition is too high, the resistance of the glass composition to acid attack is diminished. Accordingly, the glass compositions described herein generally include Al_2O_3 in an amount greater than or equal to about 2 mol. % and less than or equal to about 10 mol. %. In some embodiments, the amount of Al_2O_3 in the glass composition is greater than or equal to about 4 mol. % and less than or equal to about 8 mol. %. In some other embodiments, the amount of Al_2O_3 in the glass composition is greater than or equal to about 5 mol. % to less

than or equal to about 7 mol. %. In some other embodiments, the amount of Al_2O_3 in the glass composition is greater than or equal to about 6 mol. % to less than or equal to about 8 mol. %. In still other embodiments, the amount of Al_2O_3 in the glass composition is greater than or equal to about 5 mol. % to less than or equal to about 6 mol. %.

[0031] The glass compositions also include one or more alkali oxides such as Na_2O and/or K_2O . The alkali oxides facilitate the ion exchangeability of the glass composition and, as such, facilitate chemically strengthening the glass. The alkali oxide may include one or more of Na_2O and K_2O . The alkali oxides are generally present in the glass composition in a total concentration of Y mol. %. In some embodiments described herein, Y may be greater than about 2 mol. % and less than or equal to about 18 mol. %. In some other embodiments, Y may be greater than about 8 mol. %, greater than about 9 mol. %, greater than about 10 mol. % or even greater than about 11 mol. %. For example, in some embodiments described herein Y is greater than or equal to about 8 mol. % and less than or equal to about 18 mol. %. In still other embodiments, Y may be greater than or equal to about 9 mol. % and less than or equal to about 14 mol. %.

[0032] The ion exchangeability of the glass composition is primarily imparted to the glass composition by the amount of the alkali oxide Na_2O initially present in the glass composition prior to ion exchange. Accordingly, in the embodiments of the glass compositions described herein, the alkali oxide present in the glass composition includes at least Na_2O . Specifically, in order to achieve the desired compressive strength and depth of layer in the glass composition upon ion exchange strengthening, the glass compositions include Na_2O in an amount from about 2 mol. % to about 15 mol. % based on the molecular weight of the glass composition. In some embodiments the glass composition includes at least about 8 mol. % of Na_2O based on the molecular weight of the glass composition. For example, the concentration of Na_2O may be greater than 9 mol. %, greater than 10 mol. % or even greater than 11 mol. %. In some embodiments, the concentration of Na_2O may be greater than or equal to 9 mol. % or even greater than or equal to 10 mol. %. For example, in some embodiments the glass composition may include Na_2O in an amount greater than or equal to about 9 mol. % and less than or equal to about 15 mol. % or even greater than or equal to about 9 mol. % and less than or equal to 13 mol. %.

[0033] As noted above, the alkali oxide in the glass composition may further include K_2O . The amount of K_2O present in the glass composition also relates to the ion exchangeability of the glass composition. Specifically, as the amount of K_2O present in the glass composition increases, the compressive stress obtainable through ion exchange decreases as a result of the exchange of potassium and sodium ions. Accordingly, it is desirable to limit the amount of K_2O present in the glass composition. In some embodiments, the amount of K_2O is greater than or equal to 0 mol. % and less than or equal to 3 mol. %. In some embodiments, the amount of K_2O is less or equal to 2 mol. % or even less than or equal to 1.0 mol. %. In embodiments where the glass composition includes K_2O , the K_2O may be present in a concentration greater than or equal to about 0.01 mol. % and less than or equal to about 3.0 mol. % or even greater than or equal to about 0.01 mol. % and less than or equal to about 2.0 mol. %. In some embodiments, the amount of K_2O present in the glass composition is greater than or equal to about 0.01 mol. % and less than or equal to about 1.0 mol. %. Accordingly, it should

be understood that K_2O need not be present in the glass composition. However, when K_2O is included in the glass composition, the amount of K_2O is generally less than about 3 mol. % based on the molecular weight of the glass composition.

[0034] The alkaline earth oxides present in the composition improve the meltability of the glass batch materials and increase the chemical durability of the glass composition. In the glass compositions described herein, the total mol. % of alkaline earth oxides present in the glass compositions is generally less than the total mol. % of alkali oxides present in the glass compositions in order to improve the ion exchangeability of the glass composition. In the embodiments described herein, the glass compositions generally include from about 3 mol. % to about 13 mol. % of alkaline earth oxide. In some of these embodiments, the amount of alkaline earth oxide in the glass composition may be from about 4 mol. % to about 8 mol. % or even from about 4 mol. % to about 7 mol. %.

[0035] The alkaline earth oxide in the glass composition may include MgO , CaO , SrO , BaO or combinations thereof. In some embodiments, the alkaline earth oxide includes MgO , CaO or combinations thereof. For example, in the embodiments described herein the alkaline earth oxide includes MgO . MgO is present in the glass composition in an amount which is greater than or equal to about 3 mol. % and less than or equal to about 8 mol. % MgO . In some embodiments, MgO may be present in the glass composition in an amount which is greater than or equal to about 3 mol. % and less than or equal to about 7 mol. % or even greater than or equal to 4 mol. % and less than or equal to about 7 mol. % by molecular weight of the glass composition.

[0036] In some embodiments, the alkaline earth oxide may further include CaO . In these embodiments CaO is present in the glass composition in an amount from about 0 mol. % to less than or equal to 6 mol. % by molecular weight of the glass composition. For example, the amount of CaO present in the glass composition may be less than or equal to 5 mol. %, less than or equal to 4 mol. %, less than or equal to 3 mol. %, or even less than or equal to 2 mol. %. In some of these embodiments, CaO may be present in the glass composition in an amount greater than or equal to about 0.1 mol. % and less than or equal to about 1.0 mol. %. For example, CaO may be present in the glass composition in an amount greater than or equal to about 0.2 mol. % and less than or equal to about 0.7 mol. % or even in an amount greater than or equal to about 0.3 mol. % and less than or equal to about 0.6 mol. %.

[0037] In the embodiments described herein, the glass compositions are generally rich in MgO , (i.e., the concentration of MgO in the glass composition is greater than the concentration of the other alkaline earth oxides in the glass composition including, without limitation, CaO). Forming the glass composition such that the glass composition is MgO -rich improves the hydrolytic resistance of the resultant glass, particularly following ion exchange strengthening. Moreover, glass compositions which are MgO -rich generally exhibit improved ion exchange performance relative to glass compositions which are rich in other alkaline earth oxides. Specifically, glasses formed from MgO -rich glass compositions generally have a greater diffusivity than glass compositions which are rich in other alkaline earth oxides, such as CaO . The greater diffusivity enables the formation of a deeper depth of layer in the glass. MgO -rich glass compositions also enable a higher compressive stress to be achieved in the

surface of the glass compared to glass compositions which are rich in other alkaline earth oxides such as CaO . In addition, it is generally understood that as the ion exchange process proceeds and alkali ions penetrate more deeply into the glass, the maximum compressive stress achieved at the surface of the glass may decrease with time. However, glasses formed from glass compositions which are MgO -rich exhibit a lower reduction in compressive stress than glasses formed from glass compositions that are CaO -rich or rich in other alkaline earth oxides (i.e., glasses which are MgO -poor). Thus, MgO -rich glass compositions enable glasses which have higher compressive stress at the surface and greater depths of layer than glasses which are rich in other alkaline earth oxides.

[0038] In order to fully realize the benefits of MgO in the glass compositions described herein, it has been determined that the ratio of the concentration of CaO to the sum of the concentration of CaO and the concentration of MgO in mol. % (i.e., $(CaO)/(CaO+MgO)$) should be minimized. Specifically, it has been determined that $(CaO)/(CaO+MgO)$ should be less than or equal to 0.5. In some embodiments $(CaO)/(CaO+MgO)$ is less than or equal to 0.3 or even less than or equal to 0.2. In some other embodiments $(CaO)/(CaO+MgO)$ may even be less than or equal to 0.1.

[0039] Boron oxide (B_2O_3) is a flux which may be added to glass compositions to reduce the viscosity at a given temperature (e.g., the strain, anneal and softening temperatures) thereby improving the formability of the glass. However, it has been found that additions of boron significantly decrease the diffusivity of sodium and potassium ions in the glass composition which, in turn, adversely impacts the ion exchange performance of the resultant glass. In particular, it has been found that additions of boron significantly increase the time required to achieve a given depth of layer relative to glass compositions which are boron free. Accordingly, in some embodiments described herein, the amount of boron added to the glass composition is minimized in order to improve the ion exchange performance of the glass composition.

[0040] For example, it has been determined that the impact of boron on the ion exchange performance of a glass composition can be mitigated by controlling the ratio of the concentration of B_2O_3 to the difference between the total concentration of the alkali oxides (i.e., R_2O , where R is the alkali metals) and alumina (i.e., B_2O_3 (mol. %)/(R_2O (mol. %)- Al_2O_3 (mol. %))). In particular, it has been determined that when the ratio of $B_2O_3/(R_2O-Al_2O_3)$ is greater than or equal to about 0 and less than about 0.3 or even less than about 0.2, the diffusivities of alkali oxides in the glass compositions are not diminished and, as such, the ion exchange performance of the glass composition is maintained. Accordingly, in some embodiments, the ratio of $B_2O_3/(R_2O-Al_2O_3)$ is greater than 0 and less than or equal to 0.3. In some of these embodiments, the ratio of $B_2O_3/(R_2O-Al_2O_3)$ is greater than 0 and less than or equal to 0.2. In some embodiments, the ratio of $B_2O_3/(R_2O-Al_2O_3)$ is greater than 0 and less than or equal to 0.15 or even less than or equal to 0.1. In some other embodiments, the ratio of $B_2O_3/(R_2O-Al_2O_3)$ may be greater than 0 and less than or equal to 0.05. Maintaining the ratio $B_2O_3/(R_2O-Al_2O_3)$ to be less than or equal to 0.3 or even less than or equal to 0.2 permits the inclusion of B_2O_3 to lower the strain point, anneal point and softening point of the glass composition without the B_2O_3 adversely impacting the ion exchange performance of the glass.

[0041] In the embodiments described herein, the concentration of B_2O_3 in the glass composition is generally less than or equal to about 4 mol. %, less than or equal to about 3 mol. %, less than or equal to about 2 mol. %, or even less than or equal to 1 mol. %. For example, in embodiments where B_2O_3 is present in the glass composition, the concentration of B_2O_3 may be greater than about 0.01 mol. % and less than or equal to 4 mol. %. In some of these embodiments, the concentration of B_2O_3 may be greater than about 0.01 mol. % and less than or equal to 3 mol. %. In some embodiments, the B_2O_3 may be present in an amount greater than or equal to about 0.01 mol. % and less than or equal to 2 mol. %, or even less than or equal to 1.5 mol. %. Alternatively, the B_2O_3 may be present in an amount greater than or equal to about 1 mol. % and less than or equal to 4 mol. %, greater than or equal to about 1 mol. % and less than or equal to 3 mol. % or even greater than or equal to about 1 mol. % and less than or equal to 2 mol. %. In some of these embodiments, the concentration of B_2O_3 may be greater than or equal to about 0.1 mol. % and less than or equal to 1.0 mol. %.

[0042] While in some embodiments the concentration of B_2O_3 in the glass composition is minimized to improve the forming properties of the glass without detracting from the ion exchange performance of the glass, in some other embodiments the glass compositions are free from boron and compounds of boron such as B_2O_3 . Specifically, it has been determined that forming the glass composition without boron or compounds of boron improves the ion exchangeability of the glass compositions by reducing the process time and/or temperature required to achieve a specific value of compressive stress and/or depth of layer.

[0043] In some embodiments of the glass compositions described herein, the glass compositions are free from phosphorous and compounds containing phosphorous including, without limitation, P_2O_5 . Specifically, it has been determined that formulating the glass composition without phosphorous or compounds of phosphorous increases the chemical durability of the glass composition.

[0044] In addition to the SiO_2 , Al_2O_3 , alkali oxides and alkaline earth oxides, the glass compositions described herein may optionally further comprise one or more fining agents such as, for example, SnO_2 , As_2O_3 , and/or Cl^- (from NaCl or the like). When a fining agent is present in the glass composition, the fining agent may be present in an amount less than or equal to about 1 mol. % or even less than or equal to about 0.4 mol. %. For example, in some embodiments the glass composition may include SnO_2 as a fining agent. In these embodiments SnO_2 may be present in the glass composition in an amount greater than about 0 mol. % and less than or equal to about 1 mol. % or even an amount greater than or equal to about 0.01 mol. % and less than or equal to about 0.30 mol. %.

[0045] Moreover, the glass compositions described herein may comprise one or more additional metal oxides to further improve the chemical durability of the glass composition. For example, the glass composition may further include ZnO, TiO_2 , or ZrO_2 , each of which further improves the resistance of the glass composition to chemical attack. In these embodiments, the additional metal oxide may be present in an amount which is greater than or equal to about 0 mol. % and less than or equal to about 2 mol. %. For example, when the additional metal oxide is ZnO, the ZnO may be present in an amount greater than or equal to 1 mol. % and less than or equal to about 2 mol. %. When the additional metal oxide is

ZrO_2 or TiO_2 , the ZrO_2 or TiO_2 may be present in an amount less than or equal to about 1 mol. %.

[0046] Based on the foregoing, it should be understood that, in a first exemplary embodiment, a glass composition may include: SiO_2 in a concentration greater than about 70 mol. % and Y mol. % alkali oxide. The alkali oxide may include Na_2O in an amount greater than about 8 mol. %. The glass composition may be free of boron and compounds of boron. The concentration of SiO_2 in this glass composition may be greater than or equal to about 72 mol. %, greater than 73 mol. % or even greater than 74 mol. %. The glass composition of this first exemplary embodiment may be free from phosphorous and compounds of phosphorous. The glass composition may also include X mol. % Al_2O_3 . When Al_2O_3 is included, the ratio of Y:X may be greater than 1. The concentration of Al_2O_3 may be greater than or equal to about 2 mol. % and less than or equal to about 10 mol. %.

[0047] The glass composition of this first exemplary embodiment may also include alkaline earth oxide in an amount from about 3 mol. % to about 13 mol. %. The alkaline earth oxide may include MgO and CaO. The CaO may be present in an amount greater than or equal to about 0.1 mol. % and less than or equal to about 1.0 mol. %. A ratio $(CaO \text{ (mol. \%)} / (CaO \text{ (mol. \%)} + MgO \text{ (mol. \%)}))$ may be less than or equal to 0.5.

[0048] In a second exemplary embodiment, a glass composition may include: greater than about 68 mol. % SiO_2 ; X mol. % Al_2O_3 ; Y mol. % alkali oxide; and B_2O_3 . The alkali oxide may include Na_2O in an amount greater than about 8 mol. %. A ratio $(B_2O_3 \text{ (mol. \%)} / (Y \text{ mol. \%} - X \text{ mol. \%}))$ may be greater than 0 and less than 0.3. The concentration of SiO_2 in this glass composition may be greater than or equal to about 72 mol. %, greater than 73 mol. % or even greater than 74 mol. %. The concentration of Al_2O_3 may be greater than or equal to about 2 mol. % and less than or equal to about 10 mol. %. In this second exemplary embodiment, the ratio of Y:X may be greater than 1. When the ratio of Y:X is greater than 1, an upper bound of the ratio of Y:X may be less than or equal to 2. The glass composition of this first exemplary embodiment may be free from phosphorous and compounds of phosphorous.

[0049] The glass composition of this second exemplary embodiment may also include alkaline earth oxide. The alkaline earth oxide may include MgO and CaO. The CaO may be present in an amount greater than or equal to about 0.1 mol. % and less than or equal to about 1.0 mol. %. A ratio $(CaO \text{ (mol. \%)} / (CaO \text{ (mol. \%)} + MgO \text{ (mol. \%)}))$ may be less than or equal to 0.5.

[0050] The concentration of B_2O_3 in this second exemplary embodiment may be greater than or equal to about 0.01 mol. % and less than or equal to about 4 mol. %.

[0051] In a third exemplary embodiment, a glass article may have a type HgB1 hydrolytic resistance according to ISO 719. The glass article may include greater than about 8 mol. % Na_2O and less than about 4 mol. % B_2O_3 . The glass article may further comprise X mol. % Al_2O_3 and Y mol. % alkali oxide. The ratio $(B_2O_3 \text{ (mol. \%)} / (Y \text{ mol. \%} - X \text{ mol. \%}))$ may be greater than 0 and less than 0.3. The glass article of this third exemplary embodiment may further include a compressive stress layer having a surface compressive stress greater than or equal to about 250 MPa. The glass article may also have at least a class S3 acid resistance according to DIN

12116; at least a class A2 base resistance according to ISO 695; and a type HGA1 hydrolytic resistance according to ISO 720.

[0052] In a fourth exemplary embodiment, a glass article may include SiO₂ in an amount greater than about 70 mol. %; X mol. % Al₂O₃; and Y mol. % alkali oxide. The alkali oxide may include Na₂O in an amount greater than about 8 mol. %. A ratio of a concentration of B₂O₃ (mol. %) in the glass article to (Y mol. %–X mol. %) may be less than 0.3. The glass article may also have a type HGB1 hydrolytic resistance according to ISO 719. The concentration of SiO₂ in the glass article of this fourth exemplary embodiment may be greater than or equal to 72 mol. % and less than or equal to about 78 mol. % or even greater than 74 mol. % and less than or equal to about 78 mol. %. The concentration of Al₂O₃ in the glass article may be greater than or equal to about 4 mol. % and less than or equal to about 8 mol. %. A ratio of Y:X may be greater than 1 and less than 2.

[0053] The glass article of this fourth exemplary embodiment may also include alkaline earth oxide in an amount from about 4 mol. % to about 8 mol. %. The alkaline earth oxide may include MgO and CaO. The CaO may be present in an amount greater than or equal to about 0.2 mol. % and less than or equal to about 0.7 mol. %. A ratio (CaO (mol. %)/(CaO (mol. %)+MgO (mol. %))) may be less than or equal to 0.5. The glass article of this fourth exemplary embodiment may have a type HGA1 hydrolytic resistance according to ISO 720.

[0054] In a fifth exemplary embodiment, a glass composition may include from about 70 mol. % to about 80 mol. % SiO₂; from about 3 mol. % to about 13 mol. % alkaline earth oxide; X mol. % Al₂O₃; and Y mol. % alkali oxide. The alkali oxide may include Na₂O in an amount greater than about 8 mol. %. A ratio of Y:X may be greater than 1. The glass composition may be free of boron and compounds of boron.

[0055] In a sixth exemplary embodiment, a glass composition may include from about 68 mol. % to about 80 mol. % SiO₂; from about 3 mol. % to about 13 mol. % alkaline earth oxide; X mol. % Al₂O₃; and Y mol. % alkali oxide. The alkali oxide may include Na₂O in an amount greater than about 8 mol. %. The glass composition of this sixth exemplary embodiment may also include B₂O₃. A ratio (B₂O₃ (mol. %)/(Y mol. %–X mol. %)) may be greater than 0 and less than 0.3. A ratio of Y:X may be greater than 1.

[0056] In a seventh exemplary embodiment, a glass composition may include from about 70 mol. % to about 80 mol. % SiO₂; from about 3 mol. % to about 13 mol. % alkaline earth oxide; X mol. % Al₂O₃; and Y mol. % alkali oxide. The amount of Al₂O₃ in the glass composition may be greater than or equal to about 2 mol. % and less than or equal to about 10 mol. %. The alkaline earth oxide may include CaO in an amount greater than or equal to about 0.1 mol. % and less than or equal to about 1.0 mol. %. The alkali oxide may include from about 0.01 mol. % to about 1.0 mol. % K₂O. A ratio of Y:X may be greater than 1. The glass composition may be free of boron and compounds of boron. The glass composition may be amenable to strengthening by ion exchange.

[0057] In a seventh exemplary embodiment, a glass composition may include SiO₂ in an amount greater than about 70 mol. % and less than or equal to about 80 mol. %; X mol. % Al₂O₃; and Y mol. % alkali oxide. The alkali oxide may include Na₂O in an amount greater than about 8 mol. %. A

ratio of a concentration of B₂O₃ (mol. %) in the glass article to (Y mol. %–X mol. %) may be less than 0.3. A ratio of Y:X may be greater than 1.

[0058] In an eighth exemplary embodiment, a glass composition may include from about 72 mol. % to about 78 mol. % SiO₂; from about 4 mol. % to about 8 mol. % alkaline earth oxide; X mol. % Al₂O₃, wherein X is greater than or equal to about 4 mol. % and less than or equal to about 8 mol. %; and Y mol. % alkali oxide, wherein the alkali oxide comprises Na₂O in an amount greater than or equal to about 9 mol. % and less than or equal to about 15 mol. %. A ratio of a concentration of B₂O₃ (mol. %) in the glass article to (Y mol. %–X mol. %) is less than 0.3. A ratio of Y:X may be greater than 1.

[0059] In a ninth exemplary embodiment, a glass article may include from about 70 mol. % to about 78 mol. % SiO₂; from about 3 mol. % to about 13 mol. % alkaline earth oxide; X mol. % Al₂O₃, wherein X is greater than or equal to 2 mol. % and less than or equal to about 10 mol. %; and Y mol. % alkali oxide, wherein the alkali oxide comprises Na₂O in an amount greater than about 8 mol. %. The alkaline earth oxide may include CaO in an amount less than or equal to about 6.0 mol. %. A ratio of Y:X may be greater than about 1. The glass article may be free of boron and compounds of boron and may include a compressive stress layer with a compressive stress greater than or equal to about 250 MPa and a depth of layer greater than or equal to about 10 μm.

[0060] In a tenth exemplary embodiment, a glass article may be formed from a glass composition comprising from about 70 mol. % to about 78 mol. % SiO₂; alkaline earth oxide, wherein the alkaline earth oxide comprises MgO and CaO and a ratio (CaO (mol. %)/(CaO (mol. %)+MgO (mol. %))) is less than or equal to 0.5; X mol. % Al₂O₃, wherein X is from about 2 mol. % to about 10 mol. %; and Y mol. % alkali oxide, wherein the alkali oxide comprises Na₂O in an amount greater than about 8 mol. % and a ratio of Y:X is greater than 1. The glass article may be ion exchange strengthened with a compressive stress greater than or equal to 250 MPa and a depth of layer greater than or equal to 10 μm. The glass article may have a type HGA1 hydrolytic resistance according to ISO 720.

[0061] As noted above, the presence of alkali oxides in the glass composition facilitates chemically strengthening the glass by ion exchange. Specifically, alkali ions, such as potassium ions, sodium ions and the like, are sufficiently mobile in the glass to facilitate ion exchange. In some embodiments, the glass composition is ion exchangeable to form a compressive stress layer having a depth of layer greater than or equal to 10 μm. In some embodiments, the depth of layer may be greater than or equal to about 25 μm or even greater than or equal to about 50 μm. In some other embodiments, the depth of the layer may be greater than or equal to 75 μm or even greater than or equal to 100 μm. In still other embodiments, the depth of layer may be greater than or equal to 10 μm and less than or equal to about 100 μm. The associated surface compressive stress may be greater than or equal to about 250 MPa, greater than or equal to 300 MPa or even greater than or equal to about 350 MPa after the glass composition is treated in a salt bath of 100% molten KNO₃ at a temperature of 350° C. to 500° C. for a time period of less than about 30 hours or even about less than 20 hours.

[0062] The glass articles formed from the glass compositions described herein may have a hydrolytic resistance of HGB2 or even HGB1 under ISO 719 and/or a hydrolytic

resistance of HGA2 or even HGA1 under ISO 720 (as described further herein) in addition to having improved mechanical characteristics due to ion exchange strengthening. In some embodiments described herein the glass articles may have compressive stress layers which extend from the surface into the glass article to a depth of layer greater than or equal to 25 μm or even greater than or equal to 35 μm . In some embodiments, the depth of layer may be greater than or equal to 40 μm or even greater than or equal to 50 μm . The surface compressive stress of the glass article may be greater than or equal to 250 MPa, greater than or equal to 350 MPa, or even greater than or equal to 400 MPa. The glass compositions described herein facilitate achieving the aforementioned depths of layer and surface compressive stresses more rapidly and/or at lower temperatures than conventional glass compositions due to the enhanced alkali ion diffusivity of the glass compositions as described hereinabove. For example, the depths of layer (i.e., greater than or equal to 25 μm) and the compressive stresses (i.e., greater than or equal to 250 MPa) may be achieved by ion exchanging the glass article in a molten salt bath of 100% KNO_3 (or a mixed salt bath of KNO_3 and NaNO_3) for a time period of less than or equal to 5 hours, or even less than or equal to 4.5 hours, at a temperature less than or equal to 500° C. or even less than or equal to 450° C. In some embodiments, the time period for achieving these depths of layer and compressive stresses may be less than or equal to 4 hours or even less than or equal to 3.5 hours. The temperature for achieving these depths of layers and compressive stresses may be less than or equal to 400° C. or even less than or equal to 350° C.

[0063] These improved ion exchange characteristics can be achieved when the glass composition has a threshold diffusivity of greater than about 16 $\mu\text{m}^2/\text{hr}$ at a temperature less than or equal to 450° C. or even greater than or equal to 20 $\mu\text{m}^2/\text{hr}$ at a temperature less than or equal to 450° C. In some embodiments, the threshold diffusivity may be greater than or equal to about 25 $\mu\text{m}^2/\text{hr}$ at a temperature less than or equal to 450° C. or even 30 $\mu\text{m}^2/\text{hr}$ at a temperature less than or equal to 450° C. In some other embodiments, the threshold diffusivity may be greater than or equal to about 35 $\mu\text{m}^2/\text{hr}$ at a temperature less than or equal to 450° C. or even 40 $\mu\text{m}^2/\text{hr}$ at a temperature less than or equal to 450° C. In still other embodiments, the threshold diffusivity may be greater than or equal to about 45 $\mu\text{m}^2/\text{hr}$ at a temperature less than or equal to 450° C. or even 50 $\mu\text{m}^2/\text{hr}$ at a temperature less than or equal to 450° C.

[0064] The glass compositions described herein may generally have a strain point greater than or equal to about 525° C. and less than or equal to about 650° C. The glasses may also have an anneal point greater than or equal to about 560° C. and less than or equal to about 725° C. and a softening point greater than or equal to about 750° C. and less than or equal to about 960° C.

[0065] In the embodiments described herein the glass compositions have a CTE of less than about $70 \times 10^{-7} \text{K}^{-1}$ or even less than about $60 \times 10^{-7} \text{K}^{-1}$. These lower CTE values improve the survivability of the glass to thermal cycling or thermal stress conditions relative to glass compositions with higher CTEs.

[0066] Further, as noted hereinabove, the glass compositions are chemically durable and resistant to degradation as determined by the DIN 12116 standard, the ISO 695 standard, and the ISO 720 standard.

[0067] Specifically, the DIN 12116 standard is a measure of the resistance of the glass to decomposition when placed in an acidic solution. In brief, the DIN 12116 standard utilizes a polished glass sample of a known surface area which is weighed and then positioned in contact with a proportional amount of boiling 6M hydrochloric acid for 6 hours. The sample is then removed from the solution, dried and weighed again. The glass mass lost during exposure to the acidic solution is a measure of the acid durability of the sample with smaller numbers indicative of greater durability. The results of the test are reported in units of half-mass per surface area, specifically mg/dm^2 . The DIN 12116 standard is broken into individual classes. Class S1 indicates weight losses of up to 0.7 mg/dm^2 ; Class S2 indicates weight losses from 0.7 mg/dm^2 up to 1.5 mg/dm^2 ; Class S3 indicates weight losses from 1.5 mg/dm^2 up to 15 mg/dm^2 ; and Class S4 indicates weight losses of more than 15 mg/dm^2 .

[0068] The ISO 695 standard is a measure of the resistance of the glass to decomposition when placed in a basic solution. In brief, the ISO 695 standard utilizes a polished glass sample which is weighed and then placed in a solution of boiling 1M $\text{NaOH}+0.5\text{M Na}_2\text{CO}_3$ for 3 hours. The sample is then removed from the solution, dried and weighed again. The glass mass lost during exposure to the basic solution is a measure of the base durability of the sample with smaller numbers indicative of greater durability. As with the DIN 12116 standard, the results of the ISO 695 standard are reported in units of mass per surface area, specifically mg/dm^2 . The ISO 695 standard is broken into individual classes. Class A1 indicates weight losses of up to 75 mg/dm^2 ; Class A2 indicates weight losses from 75 mg/dm^2 up to 175 mg/dm^2 ; and Class A3 indicates weight losses of more than 175 mg/dm^2 .

[0069] The ISO 720 standard is a measure of the resistance of the glass to degradation in purified, CO_2 -free water. In brief, the ISO 720 standard protocol utilizes crushed glass grains which are placed in contact with the purified, CO_2 -free water under autoclave conditions (121° C., 2 atm) for 30 minutes. The solution is then titrated colorimetrically with dilute HCl to neutral pH. The amount of HCl required to titrate to a neutral solution is then converted to an equivalent of Na_2O extracted from the glass and reported in $\mu\text{g Na}_2\text{O}$ per weight of glass with smaller values indicative of greater durability. The ISO 720 standard is broken into individual types. Type HGA1 is indicative of up to 62 μg extracted equivalent of Na_2O per gram of glass tested; Type HGA2 is indicative of more than 62 μg and up to 527 μg extracted equivalent of Na_2O per gram of glass tested; and Type HGA3 is indicative of more than 527 μg and up to 930 μg extracted equivalent of Na_2O per gram of glass tested.

[0070] The ISO 719 standard is a measure of the resistance of the glass to degradation in purified, CO_2 -free water. In brief, the ISO 719 standard protocol utilizes crushed glass grains which are placed in contact with the purified, CO_2 -free water at a temperature of 98° C. at 1 atmosphere for 30 minutes. The solution is then titrated colorimetrically with dilute HCl to neutral pH. The amount of HCl required to titrate to a neutral solution is then converted to an equivalent of Na_2O extracted from the glass and reported in $\mu\text{g Na}_2\text{O}$ per weight of glass with smaller values indicative of greater durability. The ISO 719 standard is broken into individual types. The ISO 719 standard is broken into individual types. Type HGB1 is indicative of up to 31 μg extracted equivalent of Na_2O ; Type HGB2 is indicative of more than 31 μg and up to

62 μg extracted equivalent of Na_2O ; Type HGB3 is indicative of more than 62 μg and up to 264 μg extracted equivalent of Na_2O ; Type HGB4 is indicative of more than 264 μg and up to 620 μg extracted equivalent of Na_2O ; and Type HGB5 is indicative of more than 620 μg and up to 1085 μg extracted equivalent of Na_2O . The glass compositions described herein have an ISO 719 hydrolytic resistance of type HGB2 or better with some embodiments having a type HGB1 hydrolytic resistance.

[0071] The glass compositions described herein have an acid resistance of at least class S3 according to DIN 12116 both before and after ion exchange strengthening with some embodiments having an acid resistance of at least class S2 or even class S1 following ion exchange strengthening. In some other embodiments, the glass compositions may have an acid resistance of at least class S2 both before and after ion exchange strengthening with some embodiments having an acid resistance of class S1 following ion exchange strengthening. Further, the glass compositions described herein have a base resistance according to ISO 695 of at least class A2 before and after ion exchange strengthening with some embodiments having a class A1 base resistance at least after ion exchange strengthening. The glass compositions described herein also have an ISO 720 type HGA2 hydrolytic resistance both before and after ion exchange strengthening with some embodiments having a type HGA1 hydrolytic resistance after ion exchange strengthening and some other embodiments having a type HGA1 hydrolytic resistance both before and after ion exchange strengthening. The glass compositions described herein have an ISO 719 hydrolytic resistance of type HGB2 or better with some embodiments having a type HGB1 hydrolytic resistance. It should be understood that, when referring to the above referenced classifications according to DIN 12116, ISO 695, ISO 720 and ISO 719, a glass composition or glass article which has "at least" a specified classification means that the performance of the glass composition is as good as or better than the specified classification. For example, a glass article which has a DIN 12116 acid resistance of "at least class S2" may have a DIN 12116 classification of either S1 or S2.

[0072] The glass compositions described herein are formed by mixing a batch of glass raw materials (e.g., powders of SiO_2 , Al_2O_3 , alkali oxides, alkaline earth oxides and the like) such that the batch of glass raw materials has the desired composition. Thereafter, the batch of glass raw materials is heated to form a molten glass composition which is subsequently cooled and solidified to form the glass composition. During solidification (i.e., when the glass composition is plastically deformable) the glass composition may be shaped using standard forming techniques to shape the glass composition into a desired final form. Alternatively, the glass article may be shaped into a stock form, such as a sheet, tube or the like, and subsequently reheated and formed into the desired final form.

[0073] The enhanced strength and chemical durability of the glass compositions described herein is desirable to many glass article applications. The glass articles formed from the glass compositions described herein may have a variety of shapes, such as, for example, sheets, tubes or non-symmetric shapes, a variety of sizes, and other geometric features for various applications. Such glass articles may be suitable for use in a wide variety of applications including, without limitation, beverage packaging, food packaging, household glassware, laboratory glassware, cosmetics packaging, structural

glazing, automobile glazing, cookware, lighting products, ornamental items, display glass, industrial tubing, or scientific instruments.

[0074] In one embodiment, the glass article may be a beverage package. Without limitation, examples of beverage packages include single serving beverage bottles (e.g., beer bottles, soda bottles, juice bottles, water bottles), wine bottles, liquor bottles, and any other container that may store a beverage. The glass articles disclosed herein may be particularly well suited as beverage containers for beverages which contain aqueous solutions, including but not limited to acidic, basic, or alcohol containing solutions. For example, the glass articles described herein may serve as a packaging container for an alcoholic beverage such as a beverage comprising about 5, about 10, about 20, about 40, about 60 or about 80 proof alcohol content. Some beverage packages may be capable of being sealed to prevent contamination of the beverage within and/or to prevent spoilage or other chemical degradation of the beverage within.

[0075] In another embodiment, the glass article may be a food package. Without limitation, examples of food packages include canning jars and any other jar or other container suitable for containing food. For example, foods commonly packaged in glass articles include, without limitation, baby food, condiments, salad dressings, and pickled foods.

[0076] In yet another embodiment, the glass article may be household glassware. Without limitation, examples of household glassware include wine glasses, pub glasses, mugs, goblets, jugs, pitchers, flasks, decanters, and any other household glassware item designed for drinking or storing beverages.

[0077] In yet another embodiment, the glass article may be laboratory glassware. Without limitation, examples of laboratory glassware include beakers, standard flasks, round bottom flasks, test tubes, petri dishes, and any other like storage container suitable for use in a laboratory.

[0078] In yet another embodiment, the glass article may be a cosmetics package. Without limitation, examples of cosmetics packages include perfume containers, cologne containers, and containers which store other scented products, for human use or otherwise, foundation containers, mascara containers, eyeshadow containers, lip gloss containers, lipstick containers, and other like cosmetic products containers.

[0079] In yet another embodiment, the glass article may be structural glazing. Without limitation, examples of structural glazing include glass for framed or unframed windows in any structure (including residential structures and commercial structures), glass for doors, such as storm doors or shower doors, or glass for any other architectural element of a structure.

[0080] In yet another embodiment, the glass article may be vehicle glazing. Without limitation, examples of vehicle glazing include glazings for automobiles, such as automobile windows (including windshields), and windows on other vehicles such as boats and airplanes. For example, the glass article may be a window that may be submerged in water (including sea water) such as windows on a nautical vessel.

[0081] In yet another embodiment, the glass article may be cookware. Without limitation, examples of cookware include any dishware such as bowls, casserole dishes, dip containers, plates, baking sheets, any other bakeware, and any other items suitable for food preparation or for serving food in or upon.

[0082] In yet another embodiment, the glass article may be a lighting product. Without limitation, examples of lighting products include fluorescent lighting tubes, light bulbs, and LED lighting.

[0083] In yet another embodiment, the glass article may an ornamental item. Without limitation, examples of ornamental items include glass tiles, glass figurines, and holiday tree ornaments. It should be understood that as used herein the term "ornamental" does not mean that the item must completely lack functionality.

[0084] In yet another embodiment, the glass article may be display glass. Without limitation, display glass includes any glass that is used in a display device, such as a television, a computer monitor, a mobile device (e.g., a mobile phone with touch screen) or any other electronic visual display. The display device may employ an LCD screen, LED backlight screen, plasma screen, a touchscreen, etc.

[0085] In yet another embodiment, the glass article may industrial tubing. Such tubing may be useful for the storage and/or transport of chemicals, especially chemicals with corrosive properties or for chemicals that must not be contaminated.

[0086] In yet another embodiment, the glass article may be glass for scientific instrument. For example, the glass article may be a thermometer, lens, etc.

[0087] The glass articles described herein may have varying transparency, translucency, and color (or lack thereof). For example, additional additives to the glass composition can change the optical properties of the glass. The glass without compositional additives may be substantially clear and colorless, such as at least as clear in appearance as traditional soda lime glass, and may be desired for a number of types of glass articles contemplated herein. For example, windows are often desired to be clear and colorless. However, colored glass may be desirable in other applications, such as a brown color for beer bottles or decorative colors for ornamental glassware.

[0088] The glass compositions described herein may be particularly useful for applications where they are in direct contact with a material that should not be contaminated by the glass of the glass article. For example, some glass compositions will degrade by flaking, sometimes known as delamination, on their outer surface that is in contact with a material. The flaking may be more likely existent or more severe in cases where the glass is contacted directly by, for example and without limitation, a material that contains water, an acidic material, a basic material, or an organic material. Glass flaking may particularly be a problem in the context of a glass article in contact with a material that will be consumed by humans, such as food or beverages.

EXAMPLES

[0089] The embodiments of the glass articles formed from glass compositions described herein will be further clarified by the following examples.

Example 1

[0090] Six exemplary inventive glass compositions (compositions A-F) were prepared. The specific compositions of each exemplary glass composition are reported below in Table 1. Multiple samples of each exemplary glass composition were produced. One set of samples of each composition was ion exchanged in a molten salt bath of 100% KNO₃ at a

temperature of 450° C. for at least 5 hours to induce a compressive layer in the surface of the sample. The compressive layer had a surface compressive stress of at least 500 MPa and a depth of layer of at least 45 μm.

[0091] The chemical durability of each exemplary glass composition was then determined utilizing the DIN 12116 standard, the ISO 695 standard, and the ISO 720 standard described above. Specifically, non-ion exchanged test samples of each exemplary glass composition were subjected to testing according to one of the DIN 12116 standard, the ISO 695 standard, or the ISO 720 standard to determine the acid resistance, the base resistance or the hydrolytic resistance of the test sample, respectively. The hydrolytic resistance of the ion exchanged samples of each exemplary composition was determined according to the ISO 720 standard. To determine the hydrolytic resistance of the ion exchanged samples, the glass was crushed to the grain size required in the ISO 720 standard, ion exchanged ion exchanged in a molten salt bath of 100% KNO₃ at a temperature of 450° C. for at least 5 hours to induce a compressive stress layer in the individual grains of glass, and then tested according to the ISO 720 standard. The average results of all samples tested are reported below in Table 1.

[0092] As shown in Table 1, exemplary glass compositions A-F all demonstrated a glass mass loss of less than 5 mg/dm² and greater than 1 mg/dm² following testing according to the DIN 12116 standard with exemplary glass composition E having the lowest glass mass loss at 1.2 mg/dm². Accordingly, each of the exemplary glass compositions were classified in at least class S3 of the DIN 12116 standard, with exemplary glass composition E classified in class S2. Based on these test results, it is believed that the acid resistance of the glass samples improves with increased SiO₂ content.

[0093] Further, exemplary glass compositions A-F all demonstrated a glass mass loss of less than 80 mg/dm² following testing according to the ISO 695 standard with exemplary glass composition A having the lowest glass mass loss at 60 mg/dm². Accordingly, each of the exemplary glass compositions were classified in at least class A2 of the ISO 695 standard, with exemplary glass compositions A, B, D and F classified in class A1. In general, compositions with higher silica content exhibited lower base resistance and compositions with higher alkali/alkaline earth content exhibited greater base resistance.

[0094] Table 1 also shows that the non-ion exchanged test samples of exemplary glass compositions A-F all demonstrated a hydrolytic resistance of at least Type HGA2 following testing according to the ISO 720 standard with exemplary glass compositions C-F having a hydrolytic resistance of Type HGA1. The hydrolytic resistance of exemplary glass compositions C-F is believed to be due to higher amounts of SiO₂ and the lower amounts of Na₂O in the glass compositions relative to exemplary glass compositions A and B.

[0095] Moreover, the ion exchanged test samples of exemplary glass compositions B-F demonstrated lower amounts of extracted Na₂O per gram of glass than the non-ion exchanged test samples of the same exemplary glass compositions following testing according to the ISO 720 standard.

TABLE 1

Composition and Properties of Exemplary Glass Compositions						
	Composition in mole %					
	A	B	C	D	E	F
SiO ₂	70.8	72.8	74.8	76.8	76.8	77.4
Al ₂ O ₃	7.5	7	6.5	6	6	7
Na ₂ O	13.7	12.7	11.7	10.7	11.6	10
K ₂ O	1	1	1	1	0.1	0.1
MgO	6.3	5.8	5.3	4.8	4.8	4.8
CaO	0.5	0.5	0.5	0.5	0.5	0.5
SnO ₂	0.2	0.2	0.2	0.2	0.2	0.2
DIN 12116 (mg/dm ²) classification	3.2	2.0	1.7	1.6	1.2	1.7
ISO 695 (mg/dm ²) classification	S3	S3	S3	S3	S2	S3
ISO 720 (ug Na ₂ O/ g glass) classification	A1	A1	A2	A1	A2	A1
ISO 720 (with IX) (ug Na ₂ O/ g glass) classification	100.7	87.0	54.8	57.5	50.7	37.7
	HGA2	HGA2	HGA1	HGA1	HGA1	HGA1
	60.3	51.9	39.0	30.1	32.9	23.3
	HGA1	HGA1	HGA1	HGA1	HGA1	HGA1

Example 2

[0096] Three exemplary inventive glass compositions (compositions G-I) and three comparative glass compositions (compositions 1-3) were prepared. The ratio of alkali oxides to alumina (i.e., Y:X) was varied in each of the compositions in order to assess the effect of this ratio on various properties of the resultant glass melt and glass. The specific compositions of each of the exemplary inventive glass compositions and the comparative glass compositions are reported in Table 2. The strain point, anneal point, and softening point of melts formed from each of the glass compositions were determined and are reported in Table 2. In addition, the coefficient of

thermal expansion (CTE), density, and stress optic coefficient (SOC) of the resultant glasses were also determined and are reported in Table 2. The hydrolytic resistance of glass samples formed from each exemplary inventive glass composition and each comparative glass composition was determined according to the ISO 720 Standard both before ion exchange and after ion exchange in a molten salt bath of 100% KNO₃ at 450° C. for 5 hours. For those samples that were ion exchanged, the compressive stress was determined with a fundamental stress meter (FSM) instrument, with the compressive stress value based on the measured stress optical coefficient (SOC). The FSM instrument couples light into and out of the birefringent glass surface. The measured birefringence is then related to stress through a material constant, the stress-optic or photoelastic coefficient (SOC or PEC) and two parameters are obtained: the maximum surface compressive stress (CS) and the exchanged depth of layer (DOL). The diffusivity of the alkali ions in the glass and the change in stress per square root of time were also determined. The diffusivity (D) of the glass is calculated from the measured depth of layer (DOL) and the ion exchange time (t) according to the relationship: $DOL \approx 1.4 \sqrt{4Dt}$. Diffusivity increases with temperature according to an Arrhenius relationship, and, as such, it is reported at a specific temperature.

TABLE 2

	Glass properties as a function of alkali to alumina ratio					
	Composition Mole %					
	G	H	I	1	2	3
SiO ₂	76.965	76.852	76.962	76.919	76.960	77.156
Al ₂ O ₃	5.943	6.974	7.958	8.950	4.977	3.997
Na ₂ O	11.427	10.473	9.451	8.468	12.393	13.277
K ₂ O	0.101	0.100	0.102	0.105	0.100	0.100
MgO	4.842	4.878	4.802	4.836	4.852	4.757
CaO	0.474	0.478	0.481	0.480	0.468	0.462
SnO ₂	0.198	0.195	0.197	0.197	0.196	0.196
Strain (° C.)	578	616	654	683	548	518
Anneal (° C.)	633	674	716	745	600	567
Softening (° C.)	892	946	1003	1042	846	798
Expansion (10 ⁻⁷ K ⁻¹)	67.3	64.3	59.3	55.1	71.8	74.6
Density (g/cm ³)	2.388	2.384	2.381	2.382	2.392	2.396
SOC (nm/mm/Mpa)	3.127	3.181	3.195	3.232	3.066	3.038
ISO720 (non-IX)	88.4	60.9	47.3	38.4	117.1	208.1
ISO720 (IX450° C.-5 hr)	25.3	26	20.5	17.8	57.5	102.5
R ₂ O/Al ₂ O ₃	1.940	1.516	1.200	0.958	2.510	3.347
CS@t = 0 (MPa)	708	743	738	655	623	502
CS/√t (MPa/hr ^{1/2})	-35	-24	-14	-7	-44	-37
D (μm ² /hr)	52.0	53.2	50.3	45.1	51.1	52.4

[0097] The data in Table 2 indicates that the alkali to alumina ratio Y:X influences the melting behavior, hydrolytic resistance, and the compressive stress obtainable through ion exchange strengthening. In particular, FIG. 1 graphically depicts the strain point, anneal point, and softening point as a function of Y:X ratio for the glass compositions of Table 2. FIG. 1 demonstrates that, as the ratio of Y:X decreases below 0.9, the strain point, anneal point, and softening point of the glass rapidly increase. Accordingly, to obtain a glass which is readily meltable and formable, the ratio Y:X should be greater than or equal to 0.9 or even greater than or equal to 1.

[0098] Further, the data in Table 2 indicates that the diffusivity of the glass compositions generally decreases with the ratio of Y:X. Accordingly, to achieve glasses that can be rapidly ion exchanged in order to reduce process times (and

costs) the ratio of Y:X should be greater than or equal to 0.9 or even greater than or equal to 1.

[0099] Moreover, FIG. 2 indicates that for a given ion exchange time and ion exchange temperature, the maximum compressive stresses are obtained when the ratio of Y:X is greater than or equal to about 0.9, or even greater than or equal to about 1, and less than or equal to about 2, specifically greater than or equal to about 1.3 and less than or equal to about 2.0. Accordingly, the maximum improvement in the load bearing strength of the glass can be obtained when the ratio of Y:X is greater than about 1 and less than or equal to about 2. It is generally understood that the maximum stress achievable by ion exchange will decay with increasing ion-exchange duration as indicated by the stress change rate (i.e., the measured compressive stress divided by the square root of the ion exchange time). FIG. 2 generally shows that the stress change rate decreases as the ratio Y:X decreases.

[0100] FIG. 3 graphically depicts the hydrolytic resistance (y-axis) as a function of the ratio Y:X (x-axis). As shown in FIG. 3, the hydrolytic resistance of the glasses generally improves as the ratio Y:X decreases.

[0101] Based on the foregoing it should be understood that glasses with good melt behavior, superior ion exchange performance, and superior hydrolytic resistance can be achieved by maintaining the ratio Y:X in the glass from greater than or equal to about 0.9, or even greater than or equal to about 1, and less than or equal to about 2.

Example 3

[0102] Three exemplary inventive glass compositions (compositions J-L) and three comparative glass compositions (compositions 4-6) were prepared. The concentration of MgO and CaO in the glass compositions was varied to produce both MgO-rich compositions (i.e., compositions J-L and 4) and CaO-rich compositions (i.e., compositions 5-6). The relative amounts of MgO and CaO were also varied such that the glass compositions had different values for the ratio (CaO/(CaO+MgO)). The specific compositions of each of the exemplary inventive glass compositions and the comparative glass compositions are reported below in Table 3. The properties of each composition were determined as described above with respect to Example 2.

TABLE 3

	Glass properties as function of CaO content					
	Composition Mole %					
	J	K	L	4	5	6
SiO ₂	76.99	77.10	77.10	77.01	76.97	77.12
Al ₂ O ₃	5.98	5.97	5.96	5.96	5.97	5.98
Na ₂ O	11.38	11.33	11.37	11.38	11.40	11.34
K ₂ O	0.10	0.10	0.10	0.10	0.10	0.10
MgO	5.23	4.79	3.78	2.83	1.84	0.09
CaO	0.07	0.45	1.45	2.46	3.47	5.12
SnO ₂	0.20	0.19	0.19	0.19	0.19	0.19
Strain (° C.)	585	579	568	562	566	561
Anneal (° C.)	641	634	620	612	611	610
Softening (° C.)	902	895	872	859	847	834
Expansion (10 ⁻⁷ K ⁻¹)	67.9	67.1	68.1	68.8	69.4	70.1
Density (g/cm ³)	2.384	2.387	2.394	2.402	2.41	2.42
SOC nm/mm/Mpa	3.12	3.08	3.04	3.06	3.04	3.01
ISO720 (non-IX)	83.2	83.9	86	86	88.7	96.9
ISO720 (IX450° C.-5 hr)	29.1		28.4	33.2	37.3	40.1
Fraction of RO as CaO	0.014	0.086	0.277	0.465	0.654	0.982
CS@t = 0 (MPa)	707	717	713	689	693	676
CS/√t (MPa/hr ^{1/2})	-36	-37	-39	-38	-43	-44
D (μm ² /hr)	57.2	50.8	40.2	31.4	26.4	20.7

[0103] FIG. 4 graphically depicts the diffusivity D of the compositions listed in Table 3 as a function of the ratio (CaO/(CaO+MgO)). Specifically, FIG. 4 indicates that as the ratio (CaO/(CaO+MgO)) increases, the diffusivity of alkali ions in the resultant glass decreases thereby diminishing the ion exchange performance of the glass. This trend is supported by the data in Table 3 and FIG. 5. FIG. 5 graphically depicts the maximum compressive stress and stress change rate (y-axes) as a function of the ratio (CaO/(CaO+MgO)). FIG. 5 indicates that as the ratio (CaO/(CaO+MgO)) increases, the maximum obtainable compressive stress decreases for a given ion exchange temperature and ion exchange time. FIG. 5 also indicates that as the ratio (CaO/(CaO+MgO)) increases, the stress change rate increases (i.e., becomes more negative and less desirable).

[0104] Accordingly, based on the data in Table 3 and FIGS. 4 and 5, it should be understood that glasses with higher diffusivities can be produced by minimizing the ratio (CaO/(CaO+MgO)). It has been determined that glasses with suitable diffusivities can be produced when the (CaO/(CaO+MgO)) ratio is less than about 0.5. The diffusivity values of the glass when the (CaO/(CaO+MgO)) ratio is less than about 0.5 decreases the ion exchange process times needed to achieve a given compressive stress and depth of layer. Alternatively, glasses with higher diffusivities due to the ratio (CaO/(CaO+MgO)) may be used to achieve a higher compressive stress and depth of layer for a given ion exchange temperature and ion exchange time.

[0105] Moreover, the data in Table 3 also indicates that decreasing the ratio (CaO/(CaO+MgO)) by increasing the MgO concentration generally improves the resistance of the glass to hydrolytic degradation as measured by the ISO 720 standard.

Example 4

[0106] Three exemplary inventive glass compositions (compositions M-O) and three comparative glass compositions (compositions 7-9) were prepared. The concentration of B₂O₃ in the glass compositions was varied from 0 mol. % to about 4.6 mol. % such that the resultant glasses had different

values for the ratio $B_2O_3/(R_2O-Al_2O_3)$. The specific compositions of each of the exemplary inventive glass compositions and the comparative glass compositions are reported below in Table 4. The properties of each glass composition were determined as described above with respect to Examples 2 and 3.

TABLE 4

Glass properties as a function of B_2O_3 content Composition Mole %						
	M	N	O	7	8	9
SiO ₂	76.860	76.778	76.396	74.780	73.843	72.782
Al ₂ O ₃	5.964	5.948	5.919	5.793	5.720	5.867
B ₂ O ₃	0.000	0.214	0.777	2.840	4.443	4.636
Na ₂ O	11.486	11.408	11.294	11.036	10.580	11.099
K ₂ O	0.101	0.100	0.100	0.098	0.088	0.098
MgO	4.849	4.827	4.801	4.754	4.645	4.817
CaO	0.492	0.480	0.475	0.463	0.453	0.465
SnO ₂	0.197	0.192	0.192	0.188	0.183	0.189
Strain (° C.)	579	575	572	560	552	548
Anneal (° C.)	632	626	622	606	597	590
Softening (° C.)	889	880	873	836	816	801
Expansion (10 ⁻⁷ K ⁻¹)	68.3	67.4	67.4	65.8	64.1	67.3
Density (g/cm ³)	2.388	2.389	2.390	2.394	2.392	2.403
SOC (nm/mm/MPa)	3.13	3.12	3.13	3.17	3.21	3.18
ISO720 (non-IX)	86.3	78.8	68.5	64.4	52.7	54.1
ISO720 (IX450° C.-5 hr)	32.2	30.1	26	24.7	22.6	26.7
$B_2O_3/(R_2O-Al_2O_3)$	0.000	0.038	0.142	0.532	0.898	0.870
CS@t = 0 (MPa)	703	714	722	701	686	734
CS√t (MPa/hr ^{1/2})	-38	-38	-38	-33	-32	-39
D (μm ² /hr)	51.7	43.8	38.6	22.9	16.6	15.6

[0107] FIG. 6 graphically depicts the diffusivity D (y-axis) of the glass compositions in Table 4 as a function of the ratio $B_2O_3/(R_2O-Al_2O_3)$ (x-axis) for the glass compositions of Table 4. As shown in FIG. 6, the diffusivity of alkali ions in the glass generally decreases as the ratio $B_2O_3/(R_2O-Al_2O_3)$ increases.

[0108] FIG. 7 graphically depicts the hydrolytic resistance according to the ISO 720 standard (y-axis) as a function of the ratio $B_2O_3/(R_2O-Al_2O_3)$ (x-axis) for the glass compositions of Table 4. As shown in FIG. 6, the hydrolytic resistance of the glass compositions generally improves as the ratio $B_2O_3/(R_2O-Al_2O_3)$ increases.

[0109] Based on FIGS. 6 and 7, it should be understood that minimizing the ratio $B_2O_3/(R_2O-Al_2O_3)$ improves the diffusivity of alkali ions in the glass thereby improving the ion exchange characteristics of the glass. Further, increasing the ratio $B_2O_3/(R_2O-Al_2O_3)$ also generally improves the resistance of the glass to hydrolytic degradation. In addition, it has been found that the resistance of the glass to degradation in acidic solutions (as measured by the DIN 12116 standard) generally improves with decreasing concentrations of B_2O_3 . Accordingly, it has been determined that maintaining the ratio $B_2O_3/(R_2O-Al_2O_3)$ to less than or equal to about 0.3 provides the glass with improved hydrolytic and acid resistances as well as providing for improved ion exchange characteristics.

[0110] Based on the foregoing, it should now be understood that various aspects of glass compositions that may form glass articles are disclosed. According to a first aspect, a glass composition may include: SiO₂ in a concentration greater than about 70 mol. % and Y mol. % alkali oxide. The alkali

oxide may include Na₂O in an amount greater than about 8 mol. %. The glass composition may be free of boron and compounds of boron.

[0111] In a second aspect, the glass composition of the first aspect includes SiO₂ in an amount greater than or equal to about 72 mol. %.

[0112] In a third aspect, the glass composition of the first or second aspects is free from phosphorous and compounds of phosphorous.

[0113] In a fourth aspect, the glass composition of any of the first through third aspects further includes X mol. % Al₂O₃, wherein a ratio of Y:X is greater than 1.

[0114] In a fifth aspect, the glass composition of the ratio of Y:X in the fourth aspect is less than or equal to 2.

[0115] In a sixth aspect, the glass composition of the amount of Al₂O₃ in the fourth or fifth aspects is greater than or equal to about 2 mol. % and less than or equal to about 10 mol. %.

[0116] In a seventh aspect, the glass composition of any of the first through fifth aspects further includes from about 3 mol. % to about 13 mol. % alkaline earth oxide.

[0117] In an eighth aspect, the alkaline earth oxide of the seventh aspect includes MgO and CaO, the CaO is present in an amount greater than or equal to about 0.1 mol. % and less than or equal to about 1.0 mol. %, and a ratio (CaO (mol. %)/(CaO (mol. %)+MgO (mol. %))) is less than or equal to 0.5.

[0118] In a ninth aspect, a glass composition may include greater than about 68 mol. % SiO₂; X mol. % Al₂O₃ and Y mol. % alkali oxide; and B₂O₃. The alkali oxide may include Na₂O in an amount greater than about 8 mol. %. A ratio (B₂O₃ (mol. %)/(Y mol. %-X mol. %)) may be greater than 0 and less than 0.3.

[0119] In a tenth aspect, the glass composition of the ninth aspect includes SiO₂ in an amount greater than or equal to about 72 mol. %.

[0120] In an eleventh aspect, the glass composition of the ninth aspect or the tenth aspect includes B_2O_3 in an amount greater than or equal to about 0.01 mol. % and less than or equal to about 4 mol. %.

[0121] In a twelfth aspect, the glass composition of any of the ninth through eleventh aspects, wherein the glass composition has a ratio of Y:X is greater than 1.

[0122] In a thirteenth aspect, the ratio of Y:X of the twelfth aspect is less than or equal to 2.

[0123] A fourteenth aspect includes the glass composition of any of the ninth through thirteenth aspects wherein X is greater than or equal to about 2 mol. % and less than or equal to about 10 mol. %.

[0124] A fifteenth aspect includes the glass composition of any of the ninth through fourteenth aspects wherein the glass composition is free from phosphorous and compounds of phosphorous.

[0125] A sixteenth aspect includes the glass composition of any of the ninth through fifteenth aspects, wherein the glass composition further comprises MgO and CaO, the CaO is present in an amount greater than or equal to about 0.1 mol. % and less than or equal to about 1.0 mol. %, and a ratio $(CaO \text{ (mol. \%)} / (CaO \text{ (mol. \%)} + MgO \text{ (mol. \%)}))$ is less than or equal to 0.5.

[0126] In a seventeenth aspect, a glass article may have a type HGB1 hydrolytic resistance according to ISO 719. The glass article may include greater than about 8 mol. % Na_2O and less than about 4 mol. % B_2O_3 .

[0127] In an eighteenth aspect, the glass article of the seventeenth aspect further comprises X mol. % Al_2O_3 and Y mol. % alkali oxide, wherein a ratio $(B_2O_3 \text{ (mol. \%)} / (Y \text{ mol. \%} - X \text{ mol. \%}))$ is greater than 0 and less than 0.3.

[0128] In a nineteenth aspect, the glass article of any of the seventeenth through eighteenth aspects further comprises a compressive stress layer having a surface compressive stress greater than or equal to about 250 MPa.

[0129] A twentieth aspect includes the glass article of any of the seventeenth through nineteenth aspects, wherein the glass article has at least a class S3 acid resistance according to DIN 12116.

[0130] A twenty-first aspect includes the glass article of any of the seventeenth through twentieth aspect in which the glass article has at least a class A2 base resistance according to ISO 695.

[0131] A twenty-second aspect includes the glass article of any of the seventeenth through twenty-first aspects wherein the glass article has a type HGA1 hydrolytic resistance according to ISO 720.

[0132] In a twenty-third aspect, a glass article may include: SiO_2 in an amount greater than about 70 mol. %; X mol. % Al_2O_3 ; and Y mol. % alkali oxide. The alkali oxide may include Na_2O in an amount greater than about 8 mol. %. A ratio of a concentration of B_2O_3 (mol. %) in the glass article to $(Y \text{ mol. \%} - X \text{ mol. \%})$ may be less than 0.3. The glass article may also have a type HGB1 hydrolytic resistance according to ISO 719.

[0133] A twenty-fourth aspect includes the glass article of the twenty-third aspect wherein the amount of SiO_2 is greater than or equal to 72 mol. % and less than or equal to about 78 mol. %.

[0134] A twenty-fifth aspect includes the glass article of the twenty-third through twenty-fourth aspects wherein X is greater than or equal to about 4 mol. % and less than or equal to about 8 mol. %.

[0135] A twenty-sixth aspect includes the glass article of the twenty-third through twenty-fifth aspects wherein a ratio of Y:X is greater than 1.

[0136] A twenty-seventh aspect includes the glass article of the twenty-third through twenty-sixth aspects, wherein a ratio of Y:X is less than 2.

[0137] A twenty-eighth aspect includes the glass article of the twenty-third through twenty-seventh aspects which further comprises from about 4 mol. % to about 8 mol. % alkaline earth oxide.

[0138] A twenty-ninth aspect includes the glass article of the twenty-third through twenty-eighth aspects which the further comprises MgO and CaO, CaO is present in an amount greater than or equal to about 0.2 mol. % and less than or equal to about 0.7 mol. % and a ratio $(CaO \text{ (mol. \%)} / (CaO \text{ (mol. \%)} + MgO \text{ (mol. \%)}))$ is less than or equal to 0.5.

[0139] A thirtieth aspect includes the glass article of the twenty-third through twenty-ninth aspects, wherein the glass article has a type HGA1 hydrolytic resistance according to ISO 720.

[0140] In a thirty-first aspect, a glass composition may include from about 70 mol. % to about 80 mol. % SiO_2 ; from about 3 mol. % to about 13 mol. % alkaline earth oxide; X mol. % Al_2O_3 ; and Y mol. % alkali oxide. The alkali oxide may include Na_2O in an amount greater than about 8 mol. %. A ratio of Y:X may be greater than 1 and the glass composition may be free of boron and compounds of boron.

[0141] In a thirty-second aspect, a glass composition may include: from about 72 mol. % to about 78 mol. % SiO_2 ; from about 4 mol. % to about 8 mol. % alkaline earth oxide; X mol. % Al_2O_3 ; and Y mol. % alkali oxide. The amount of alkaline earth oxide may be greater than or equal to about 4 mol. % and less than or equal to about 8 mol. %. The alkali oxide may include Na_2O in an amount greater than or equal to about 9 mol. % and less than or equal to about 15 mol. %. A ratio of Y:X may be greater than 1. The glass composition may be free of boron and compounds of boron.

[0142] In a thirty-third aspect, a glass composition may include: from about 68 mol. % to about 80 mol. % SiO_2 ; from about 3 mol. % to about 13 mol. % alkaline earth oxide; X mol. % Al_2O_3 ; and Y mol. % alkali oxide. The alkali oxide may include Na_2O in an amount greater than about 8 mol. %. The glass composition may also include B_2O_3 . A ratio $(B_2O_3 \text{ (mol. \%)} / (Y \text{ mol. \%} - X \text{ mol. \%}))$ may be greater than 0 and less than 0.3, and a ratio of Y:X may be greater than 1.

[0143] In a thirty-fourth aspect, a glass composition may include from about 70 mol. % to about 80 mol. % SiO_2 ; from about 3 mol. % to about 13 mol. % alkaline earth oxide; X mol. % Al_2O_3 ; and Y mol. % alkali oxide. The alkaline earth oxide may include CaO in an amount greater than or equal to about 0.1 mol. % and less than or equal to about 1.0 mol. %. X may be greater than or equal to about 2 mol. % and less than or equal to about 10 mol. %. The alkali oxide may include from about 0.01 mol. % to about 1.0 mol. % K_2O . A ratio of Y:X may be greater than 1. The glass composition may be free of boron and compounds of boron.

[0144] In a thirty-fifth aspect, a glass composition may include SiO_2 in an amount greater than about 70 mol. % and less than or equal to about 80 mol. %; from about 3 mol. % to about 13 mol. % alkaline earth oxide; X mol. % Al_2O_3 ; and Y mol. % alkali oxide. The alkali oxide may include Na_2O in an amount greater than about 8 mol. %. A ratio of a concentration

of B_2O_3 (mol. %) in the glass composition to (Y mol. %–X mol. %) may be less than 0.3. A ratio of Y:X may be greater than 1.

[0145] In a thirty-sixth aspect, the glass composition of any of the thirty-first through thirty-fifth aspects wherein the SiO_2 is present in an amount less than or equal to 78 mol. %.

[0146] A thirty-seventh aspect includes the glass composition of any of thirty-first through thirty-sixth aspects, wherein an amount of the alkaline earth oxide is greater than or equal to about 4 mol. % and less than or equal to about 8 mol. %.

[0147] A thirty-eighth aspect includes the glass composition of any of the thirty-first through thirty-seventh aspects wherein the alkaline earth oxide comprises MgO and CaO and a ratio $(CaO \text{ (mol. \%)} / (CaO \text{ (mol. \%)} + MgO \text{ (mol. \%)}))$ is less than or equal to 0.5.

[0148] A thirty-ninth aspect includes the glass composition of any of the thirty-first through thirty eighth aspects, wherein the alkaline earth oxide comprises from about 0.1 mol. % to less than or equal to about 1.0 mol. % CaO.

[0149] A fortieth aspect includes, the glass composition of any of the thirty-first through thirty-ninth aspects wherein the alkaline earth oxide comprises from about 3 mol. % to about 7 mol. % MgO.

[0150] A forty-first aspect includes the glass composition of any of the thirty-first, thirty-second, or thirty-fourth aspects, wherein X is greater than or equal to about 2 mol. % and less than or equal to about 10 mol. %.

[0151] A forty-second aspect includes the glass composition of any of the thirty-first through forty-first aspects, wherein the alkali oxide comprises greater than or equal to about 9 mol. % Na_2O and less than or equal to about 15 mol. % Na_2O .

[0152] A forty-third aspect includes the glass composition of any of the thirty-first through forty-second aspects, wherein the ratio of Y:X is less than or equal to 2.

[0153] A forty-fourth aspect includes the glass composition of any of the thirty-first through forty-third aspects, wherein the ratio of Y:X is greater than or equal to 1.3 and less than or equal to 2.0.

[0154] A forty-fifth aspect includes the glass composition of any of the thirty-first through forty-fourth aspects, wherein the alkali oxide further comprises K_2O in an amount less than or equal to about 3 mol. %.

[0155] A forty-sixth aspect includes the glass composition of any of the thirty-first through forty-fifth aspects, wherein the glass composition is free of phosphorous and compounds of phosphorous.

[0156] A forty-seventh includes the glass composition of any of the thirty-first through forty-sixth aspects, wherein the alkali oxide comprises K_2O in an amount greater than or equal to about 0.01 mol. % and less than or equal to about 1.0 mol. %.

[0157] A forty-eighth aspect includes the glass composition of any of the thirty-second or thirty-fourth aspects, wherein an amount of SiO_2 is greater than or equal to about 70 mol. %.

[0158] A forty-ninth aspect includes the glass composition of any of the thirty-second or thirty-fourth aspects, wherein the ratio $(B_2O_3 \text{ (mol. \%)} / (Y \text{ mol. \%} - X \text{ mol. \%}))$ is less than 0.2.

[0159] A fiftieth aspect includes the glass composition of any of the thirty-second or thirty-fourth aspects, wherein an amount of B_2O_3 is less than or equal to about 4.0 mol. %.

[0160] A fifty-first aspect includes the glass composition of the fiftieth aspect, wherein the amount of B_2O_3 is greater than or equal to about 0.01 mol. %.

[0161] A fifty-second aspect includes the glass composition of the thirty-fourth aspect, wherein the glass composition is free from boron and compounds of boron.

[0162] A fifty-third aspect includes the glass composition of any of the thirty-first through thirty-fourth aspects, wherein the concentration of SiO_2 is greater than or equal to about 72 mol. %.

[0163] A fifty-fourth aspect includes the glass composition of any of the thirty-first through fifty-third aspects, wherein the concentration of SiO_2 is greater than or equal to about 73 mol. %.

[0164] In a fifty-fifth aspects, a glass article is formed from the glass composition of any of the thirty-first through fifty-fourth aspects.

[0165] A fifty-sixth aspect includes the glass article of the fifty-fifth aspect, wherein the glass article has a type HGB1 hydrolytic resistance according to ISO 719.

[0166] A fifty-seventh aspect includes the glass article of any of the fifty-fifth through fifty-sixth aspects, wherein the glass article has a type HGA1 hydrolytic resistance according to ISO 720 after ion exchange strengthening.

[0167] A fifty-eighth aspect includes the glass article of any of the fifty-fifth through fifty-seventh aspects, wherein the glass article has a type HGA1 hydrolytic resistance according to ISO 720 before and after ion exchange strengthening.

[0168] A fifty-ninth aspect includes the glass article of any of the fifty-fifth through fifty-eighth aspects, wherein the glass article has at least a class S3 acid resistance according to DIN 12116.

[0169] A sixtieth aspect includes, the glass article of any of the fifty-fifth through fifty-ninth aspects, wherein the glass article has at least a class A2 base resistance according to ISO 695.

[0170] A sixty-first aspect includes the glass article of any of the fifty-fifth through sixtieth aspects, wherein the glass article is a beverage package, a food package, household glassware, laboratory glassware, a cosmetics package, structural glazing, automobile glazing, cookware, a lighting product, an ornamental item, display glass, industrial tubing, or a scientific instrument.

[0171] A sixty-second aspect includes the glass article of any of the fifty-fifth through sixty-first aspects, wherein the glass article is ion exchange strengthened.

[0172] A sixty-third aspect includes the glass article of any of the fifty-fifth through sixty-second aspects in which the glass article further a compressive stress layer with a depth of layer greater than or equal to $10 \mu m$ and a surface compressive stress greater than or equal to 250 MPa.

[0173] In a sixty-fourth aspect, a glass article may have a type HGB1 hydrolytic resistance according to ISO 719. The glass article may also have a threshold diffusivity of greater than $16 \mu m^2/hr$ at a temperature less than or equal to $450^\circ C$.

[0174] A sixty-fifth aspect includes the glass article of the sixty-fourth aspect wherein the threshold diffusivity is greater than or equal to $20 \mu m^2/hr$ at a temperature of less than or equal to $450^\circ C$.

[0175] A sixty-sixth aspect includes the glass article of any of the sixty-third through sixty-fourth aspects wherein the glass article has a type HGA1 hydrolytic resistance according to ISO 720 after ion exchange strengthening.

[0176] A sixty-seventh aspect includes the glass article of any of the sixty-fourth through sixty-sixth aspects which further comprises a compressive stress with a depth of layer greater than 25 μm .

[0177] A sixty-eighth aspect includes the glass article of the sixty-seventh aspect wherein the depth of layer is greater than 35 μm .

[0178] A sixty-ninth aspect includes the glass article of any of the sixty-third through sixty-eighth aspects wherein the glass article is ion exchange strengthened and the ion exchange strengthening comprises treating the glass article in a molten salt bath for a time less than or equal to 5 hours at a temperature less than or equal to 450° C.

[0179] A seventieth aspect includes the glass article of any of the sixty-third through sixty-ninth aspects which further comprises a surface compressive stress greater than or equal to 350 MPa.

[0180] A seventy-first aspect includes the glass article of any of the sixty-third through seventieth aspects wherein the surface compressive stress is greater than or equal to 400 MPa.

[0181] A seventy-second aspect includes the glass article of any of the sixty-third through seventy-first aspects, wherein the glass article is ion exchange strengthened and the ion exchange strengthening comprises treating the glass article in a molten salt bath for a time less than or equal to 5 hours at a temperature less than or equal to 450° C.

[0182] A seventy-second aspect includes the glass article of any of the sixty-third through seventy-second aspects, wherein the glass article is a beverage package, a food package, household glassware, laboratory glassware, a cosmetics package, structural glazing, automobile glazing, cookware, a lighting product, an ornamental item, display glass, industrial tubing, or a scientific instrument.

[0183] In a seventy-third aspect, a glass article may have a type HGB1 hydrolytic resistance according to ISO 719. The glass article may also have a compressive stress layer with a depth of layer of greater than 25 μm and a surface compressive stress of greater than or equal to 350 MPa. The glass article may be ion exchange strengthened and the ion exchange strengthening may include treating the glass article in a molten salt bath for a time less than or equal to 5 hours at a temperature less than or equal to 450° C.

[0184] A seventy-fourth aspect includes, the glass article of the seventy-third aspect, wherein the glass article has a type HGA1 hydrolytic resistance according to ISO 720 after ion exchange strengthening.

[0185] A seventy-fifth aspect includes the glass article of any of the seventy-third through seventy-fourth aspects, wherein the glass article has a threshold diffusivity of greater than 16 $\mu\text{m}^2/\text{hr}$ at a temperature of less than or equal to 450° C.

[0186] A seventy-sixth aspect includes the glass article of any of the seventy-third through seventy-fifth aspects, wherein the threshold diffusivity is greater than or equal to 20 $\mu\text{m}^2/\text{hr}$ at a temperature of less than or equal to 450° C.

[0187] A seventy-seventh aspect includes the glass article of any of the seventy-third through seventy-sixth aspects, wherein the glass article is a beverage package, a food package, household glassware, laboratory glassware, a cosmetics package, structural glazing, automobile glazing, cookware, a lighting product, an ornamental item, display glass, industrial tubing, or a scientific instrument.

[0188] It will be apparent to those skilled in the art that various modifications and variations can be made to the embodiments described herein without departing from the spirit and scope of the claimed subject matter. Thus it is intended that the specification cover the modifications and variations of the various embodiments described herein provided such modification and variations come within the scope of the appended claims and their equivalents.

What is claimed is:

1. A glass article formed from a glass composition comprising:

from about 70 mol. % to about 78 mol. % SiO_2 ;

from about 3 mol. % to about 13 mol. % alkaline earth oxide;

X mol. % Al_2O_3 ;

Y mol. % alkali oxide, wherein the alkali oxide comprises Na_2O in an amount greater than or equal to about 9 mol. % and less than or equal to about 15 mol. %, and wherein:

a ratio of Y:X is greater than 1;

the glass article is free of boron and compounds of boron; the glass article comprises a compressive stress layer with a compressive stress greater than or equal to about 250 MPa and depth of layer greater than or equal to about 25 μm ; and

the glass article has at least a type HGA2 hydrolytic resistance according to ISO 720.

2. The glass article of claim 1, wherein the glass article is a beverage package.

3. The glass article of claim 2, wherein the beverage package is a container for storing alcoholic beverages.

4. The glass article of claim 1, wherein the glass article is a food package.

5. The glass article of claim 1, wherein the glass article is household glassware.

6. The glass article of claim 1, wherein the glass article is laboratory glassware.

7. The glass article of claim 1, wherein the glass article is a cosmetics package.

8. The glass article of claim 1, wherein the glass article is structural glazing or vehicle glazing.

9. The glass article of claim 1, wherein the glass article is cookware.

10. The glass article of claim 1, wherein the glass article is a lighting product.

11. The glass article of claim 1, wherein the glass article is an ornamental item.

12. The glass article of claim 1, wherein the glass article is display glass.

13. The glass article of claim 1, wherein the glass article is industrial tubing.

14. The glass article of claim 1, wherein the glass article is a scientific instrument.

15. A glass article formed from a glass composition comprising:

from about 70 mol. % to about 78 mol. % SiO_2 ;

from about 3 mol. % to about 13 mol. % alkaline earth oxide, wherein the alkaline earth oxide comprises from about 0.1 mol. % to about 1.0 mol. % CaO ;

X mol. % Al_2O_3 ;

Y mol. % alkali oxide, wherein the alkali oxide comprises Na_2O in an amount greater than or equal to about 9 mol. % and less than or equal to about 15 mol. %, and wherein:

a ratio of Y:X is from about 1 to about 2;
the glass article is free of boron and compounds of boron;
the glass article comprises a compressive stress layer with
a compressive stress greater than or equal to about 250
MPa and depth of layer greater than or equal to about 25
 μm ;
the glass article has at least a type HGA2 hydrolytic resis-
tance according to ISO 720; and
the glass article is a beverage package, a food package,
household glassware, laboratory glassware, a cosmetics
package, structural glazing, automobile glazing, cook-
ware, a lighting product, an ornamental item, display
glass, industrial tubing, or a scientific instrument.

16. The glass article of claim **15**, wherein the glass article
is free of phosphorous and compounds of phosphorous.

17. The glass article of claim **15**, wherein the glass com-
position comprises from about 72 mol. % to about 78 mol. %
 SiO_2 .

18. The glass article of claim **15**, wherein the glass com-
position comprises from about 4 mol. % to about 8 mol. %
alkaline earth oxide.

19. The glass article of claim **15**, wherein the ratio of Y:X is
from about 1.3 to 2.

20. The glass article of claim **15**, wherein the alkaline earth
oxide comprises MgO and CaO and a ratio $(\text{CaO (mol. \%)} /$
 $(\text{CaO (mol. \%)} + \text{MgO (mol. \%)}))$ is less than or equal to 0.5.

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