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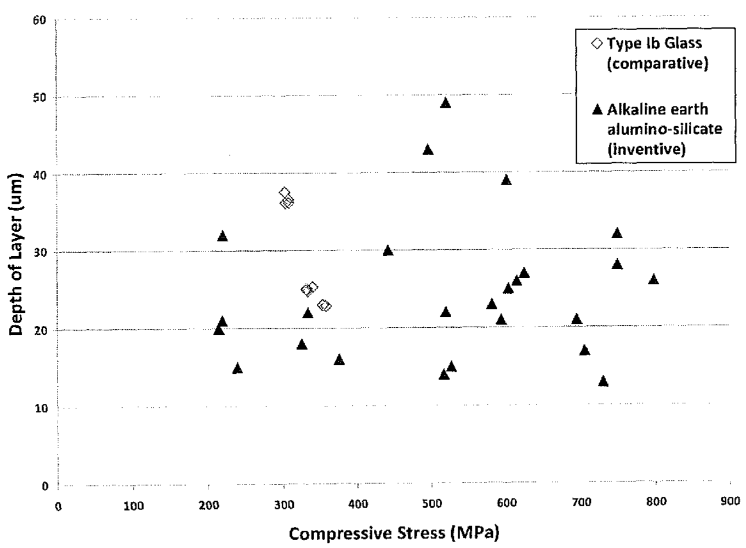
(54) **Title**: ALKALINE EARTH ALUMINO-SILICATE GLASS COMPOSITIONS WITH IMPROVED CHEMICAL AND MECHANICAL DURABILITY

FIG. 1



(57) **Abstract**: Alkaline earth alumino-silicate glass compositions with improved chemical and mechanical durability and pharmaceutical packages comprising the same are disclosed herein. In one embodiments, a glass composition includes from about 67 mol.% to about 75 mol.% SiO_2; from about 6 mol.% to about 10 mol.% Al_2O_3; from about 5 mol.% to about 12 mol.% alkali oxide; and from about 9 mol.% to about 15 mol.% of alkaline earth oxide. The alkali oxide comprises at least Na_2O and K_2O. The glass composition is free from boron and compounds of boron and is susceptible to ion exchange thereby facilitating chemically strengthening the glass to improve the mechanical durability.

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Alkaline Earth Alumino-Silicate Glass Compositions with Improved Chemical and Mechanical Durability

Cross-Reference to Related Applications

[0001] This application claims the benefit of priority under 35 U.S.C. § 119 of U.S. Provisional Application Serial No. 61/551,133 filed on October 25, 2011, the content of which is relied upon and incorporated herein by reference in its entirety.

Background

Field

[0002] The present specification generally relates to glass compositions and, more specifically, to chemically durable glass compositions which are free from boron and compounds of boron and which are suitable for use in pharmaceutical packaging.

Technical Background

[0003] Historically, glass has been used as the preferred material for packaging pharmaceuticals because of its hermeticity, optical clarity, and excellent chemical durability relative to other materials. Specifically, the glass used in pharmaceutical packaging must have adequate chemical durability so as to not affect the stability of the pharmaceutical compositions contained therein. Glasses having suitable chemical durability include those glass compositions within the ASTM standard 'Type 1a' and 'Type 1b' glass compositions which have a proven history of chemical durability.

[0004] Although Type 1a and Type 1b glass compositions are commonly used in pharmaceutical packages, they do suffer from several deficiencies. Foremost is the tendency of these glasses to phase separate. Specifically, the glass tends to separate on a fine microscopic scale into an alkali borate phase and silica rich phase. This phase separation may be a precursor to the glass flakes and de-lamination phenomena that have been reported in such glasses.

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[0005] A second deficiency is that the low levels of alkali and alumina in Type 1a and Type 1b glass compositions result in only a minimal ability to ion exchange and strengthen these glasses. As a result, pharmaceutical packages made from Type 1a and 1b pharmaceutical glasses offer poor resistance to damage from mechanical events such as impacts and scratches.

[0006] Accordingly, a need exists for glass compositions which are chemically durable and susceptible to chemical strengthening by ion exchange for use in glass pharmaceutical packages and similar applications.

[0006A] The discussion of documents, acts, materials, devices, articles and the like is included in this specification solely for the purpose of providing a context for the present invention. It is not suggested or represented that any or all of these matters formed part of the prior art base or were common general knowledge in the field relevant to the present invention as it existed before the priority date of each claim of this application.

[0006B] Where the terms "comprise", "comprises", "comprised" or "comprising" are used in this specification (including the claims) they are to be interpreted as specifying the presence of the stated features, integers, steps or components, but not precluding the presence of one or more other features, integers, steps or components, or group thereof.

SUMMARY

[0007] According to one embodiment, a glass composition may include from about 67 mol.% to about 75 mol.% SiO_2; from about 6 mol.% to about 10 mol.% Al_2O_3; from about 5 mol.% to about 12 mol.% alkali oxide; and from about 9 mol.% to about 15 mol.% of alkaline earth oxide. The alkali oxide comprises at least Na_2O and K_2O. The glass composition is free from boron and compounds of boron and is susceptible to ion exchange thereby facilitating chemically strengthening of glass to improve mechanical durability.

[0008] In another embodiment, a glass composition may include from about 67 mol.% to about 75 mol.% SiO_2; from about 6 mol.% to about 10 mol.% Al_2O_3; from about 5 mol.% to about 12 mol.% alkali oxide; and from about 9 mol.% to about 15 mol.% of alkaline earth oxide. The alkaline earth oxide comprises at least one of SrO and BaO. The glass composition is free from boron and compounds of boron and is susceptible to ion exchange thereby facilitating chemically strengthening the glass to improve mechanical durability.

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[0008A] In a further embodiment the present invention provides a glass composition comprising: from about 65 mol.% to about 75 mol.% SiO_2; from about 6 mol.% to about 12.5 mol.% Al_2O_3; from about 5 mol.% to about 12 mol.% alkali oxide, wherein the alkali oxide comprises Na_2O and K_2O and the K_2O is present in an amount less than or equal to 0.5 mol.%; and from about 8.0 mol.% to about 15 mol.% of at least one alkaline earth oxide, wherein the glass composition is susceptible to strengthening by ion-exchange.

[0008B] In yet a further embodiment, the present invention provides a glass composition comprising: from about 67 mol.% to about 75 mol.% SiO_2; from about 6 mol.% to about 10 mol.% Al_2O_3; from about 5 mol.% to about 12 mol.% alkali oxide, wherein the alkali oxide comprises K_2O in an amount less than or equal to about 0.5 mol.%; from about 8 mol.% to about 15 mol.% of alkaline earth oxide, wherein the alkaline earth oxide comprises at least one of SrO and BaO, wherein: the glass composition is free from boron and compounds of boron; the glass composition is free from phosphorous and compounds of phosphorous; and the glass composition is ion exchangeable to a depth of layer greater than or equal to about 15 μm with a corresponding compressive stress greater than or equal to about 250 MPa.

[0008C] In yet a further embodiment, the present invention provides a glass composition comprising:

from 67 mol.% to about 75 mol.% SiO_2;

from about 6 mol.% to about 10 mol.% Al_2O_3;

from about 5 mol.% to about 12 mol.% alkali oxide, wherein the alkali oxide comprises Na_2O and K_2O and the K_2O is present in an amount less than or equal to 0.5 mol.%; and

from about 9 mol.% to about 15 mol.% of alkaline earth oxide, the alkaline earth oxide comprising greater than 0 mol.% and less than or equal to 3 mol.% MgO and from about 2 mol.% to about 7 mol.% CaO, wherein a ratio of a concentration of MgO to the sum of the concentration of divalent cations (MgO:ΣRO) is less than 0.3 and

the glass composition is susceptible to strengthening by ion-exchange.

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[0008D] In yet a further embodiment, the present invention provides a glass composition comprising:

from 67 mol.% to about 75 mol.% SiO_2;

from about 6 mol.% to about 10 mol.% Al_2O_3;

from about 5 mol.% to about 12 mol.% alkali oxide, wherein the alkali oxide comprises K_2O in an amount less than or equal to about 0.5 mol.%;

from about 9 mol.% to about 15 mol.% of alkaline earth oxide, wherein the alkaline earth oxide comprises greater than about 0 mol.% and less than or equal to 3 mol.% MgO, from about 2 mol.% to about 7 mol.% CaO, at least one of SrO and BaO, wherein:

a ratio of a concentration of MgO to the sum of the concentration of divalent cations (MgO:ΣRO) is less than 0.3;

the glass composition is free from boron and compounds of boron;

the glass composition is free from phosphorous and compounds of phosphorous; and

the glass composition is ion exchangeable to a depth of layer greater than or equal to about 15 μm with a corresponding compressive stress greater than or equal to about 250 MPa.

[0008E] In yet another embodiment, the present invention provides a glass composition comprising:

from 67 mol.% to about 75 mol.% SiO_2;

from about 6 mol.% to about 10 mol.% Al_2O_3;

from about 5 mol.% to about 12 mol.% alkali oxide, wherein the alkali oxide comprises Na_2O and K_2O and the K_2O is present in an amount less than or equal to 0.5 mol.%; and

from about 9 mol.% to about 15 mol.% of alkaline earth oxide,

the glass composition is susceptible to strengthening by ion-exchange, free from boron and compounds of boron, and has a CTE less than 60×10^{-7}/K from room temperature to 300°C.

[0008F] In yet another embodiment, the present invention provides a glass composition comprising:

from 67 mol.% to about 75 mol.% SiO_2;

from about 6 mol.% to about 10 mol.% Al_2O_3;

from about 5 mol.% to about 12 mol.% alkali oxide, wherein the alkali oxide comprises K_2O in an amount less than or equal to about 0.5 mol.%;

from about 9 mol.% to about 15 mol.% of alkaline earth oxide, wherein the alkaline earth oxide comprises at least one of SrO and BaO, wherein:

the glass composition is free from boron and compounds of boron;

the glass composition has a CTE less than 60×10^{-7}/K from room temperature to 300°C; and

the glass composition is ion exchangeable to a depth of layer greater than or equal to about 15 μm and less than or equal to 50 μm with a corresponding compressive stress greater than or equal to about 200 MPa and less than or equal to 800 MPa.

[0009] In yet another embodiment, a pharmaceutical package for a pharmaceutical composition may include a glass composition comprising from about 67 mol.% to about 75 mol.% SiO_2; from about 6 mol.% to about 10 mol.% Al_2O_3; from about 5 mol.% to about 12 mol.% alkali oxide; and from about 9 mol.% to about 15 mol.% of alkaline earth oxide. The alkali oxide comprises at least Na_2O and K_2O. The composition is free from boron and compounds of boron and has at least a class S3 acid resistance according to DIN 12116; a class A1 base resistance according to ISO 695; and a type HGA1 hydrolytic resistance according to ISO 720. The pharmaceutical package may be ion exchange strengthened to improve the mechanical durability of the package.

[0010] Additional features and advantages of the embodiments 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 ion-exchange properties (compressive stress and depth of layer) for inventive glass composition and, for purposes of comparison, Type 1B glass compositions.

DETAILED DESCRIPTION

[0013] Reference will now be made in detail to various embodiments of glass compositions which exhibit improved chemical and mechanical durability. Such glass compositions are suitable for use in various applications including, without limitation, as pharmaceutical packaging materials. 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, and alkali oxides (such as Na_2O and K_2O) in amounts which impart chemical durability to the glass composition. Moreover, the alkali oxide 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.

[0014] The term "softening point," as used herein, refers to the temperature at which the viscosity of the glass composition is $1x10^{7.6}$ poise.

[0015] The term "annealing point," as used herein, refers to the temperature at which the viscosity of the glass composition is $1x10^{13}$ poise.

[0016] The term "CTE," as used herein, refers to the coefficient of thermal expansion of the glass composition over a temperature range from about RT to about 300°C.

[0017] 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 3 established material testing standards: DIN 12116 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." Each standard and the classifications within each standard are described in further detail herein.

[0018] The glass compositions described herein are alkaline earth alumino-silicate glass compositions which generally include a combination of SiO_2, Al_2O_3, at least one alkaline earth oxide, alkali oxide including at least as Na_2O and K_2O, and are 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, or the like. These components may be added as fining agents and/or to further enhance the chemical durability of the glass composition.

[0019] 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 glass network. SiO_2 enhances the chemical durability and, in particular, the resistance of the glass composition to decomposition in acid. 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. However, additions of alkali oxide assist in offsetting this effect by decreasing the softening point of the glass. In the embodiments described herein, the glass composition generally comprises SiO_2 in an amount greater than or equal to about 67 mol.% and less than or equal to about 75 mol.%. In some embodiments SiO_2 is present in the glass composition in an amount greater than or equal to about 67 mol.% and less than or equal to about 73 mol.%. In each of these embodiments, the amount of SiO_2 present in the glass composition may be greater than or equal to about 70 mol.% or even greater than or equal to about 72 mol.%.

[0020] 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. Moreover, additions of Al_2O_3 to the composition reduce the propensity of alkali constituents (such as Na and K) from leaching out of the glass and, as such, additions of Al_2O_3 increase the resistance of the composition to hydrolytic degradation. Moreover, additions of Al_2O_3 greater than about 10 mol.% may also increase the softening point of the glass thereby reducing the formability of the glass. Accordingly, the glass compositions described herein generally include Al_2O_3 in an amount greater than or equal to about 6 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 7 mol.% and less than or equal to about 10 mol.%.

[0021] The glass compositions also include at least two alkali oxides. The alkali oxides facilitate the ion exchangeability of the glass composition and, as such, facilitate chemically strengthening the glass substrate. The alkali oxides also lower the softening point of the glass thereby offsetting the increase in the softening point due to higher concentrations of SiO_2 in the glass composition. The alkali oxides also assist in improving the chemical durability of the glass composition. The alkali oxides are generally present in the glass composition in an amount greater than or equal to about 5 mol.% and less than or equal to about 12 mol.%. In some of these embodiments, the amount of alkali oxides may be greater than or equal to about 5 mol.% and less than or equal to about 10 mol.%. In some other embodiments, the amount of alkali oxide may be greater than or equal to about 5 mol.% and less than or equal to about 8 mol.%. In all the glass compositions described herein, the alkali oxides comprise at least Na_2O and K_2O. In some embodiments, the alkali oxides further comprise Li_2O.

[0022] 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. 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 greater than or equal to about 2.5 mol.% and less than or equal to about 10 mol.% based on the molecular weight of the glass composition. In some embodiments the glass composition may include Na_2O in an amount greater than or equal to about 3.5 mol.% and less than or equal to about 8 mol.%. In some of these embodiments the glass composition may include Na_2O in an amount greater than or equal to about 6 mol.% and less than or equal to about 8 mol.%.

[0023] As noted above, the alkali oxides in the glass composition also 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. 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 0 mol.% and less than or equal to about 2.5 mol.% by molecular weight of the glass composition. In some of these embodiments, the amount of K_2O present in the glass composition is less than or equal to about 0.5 mol.% by molecular weight of the glass composition.

[0024] As noted above, in some embodiments, the alkali oxide in the glass composition further comprises Li_2O. Including Li_2O in the glass composition further decreases the softening point of the glass. In embodiments where the alkali oxide includes Li_2O, the Li_2O may be present in an amount greater than or equal to about 1 mol.% and less than or equal to about 3 mol.%. In some embodiments, Li_2O may be present in the glass composition in an amount which is greater than about 2 mol.% and less than or equal to about 3 mol.%.

[0025] 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. The presence of alkaline earth oxides in the glass composition also reduce the susceptibility of the glass to de-lamination. In the glass compositions described herein, the glass compositions generally include from about 9 mol.% to about 15 mol.% of alkaline earth oxide. In some of these embodiments, the amount of alkaline earth oxide in the glass composition may be from about 10 mol.% to about 14 mol.%.

[0026] The alkaline earth oxide in the glass composition may include MgO, CaO, SrO, BaO 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 7 mol.% by molecular weight of the glass composition or even greater than or equal about 2 mol.% and less than or equal to about 5 mol.% by molecular weight of the glass composition.

[0027] In some embodiments, the alkaline earth oxide also includes CaO. In these embodiments CaO is present in the glass composition in an amount from about 3 mol.% to less than or equal to 7 mol.% by molecular weight of the glass composition. In some of these embodiments, CaO may be present in the glass composition in an amount greater than or equal to about 4 mol.% and less than or equal to about 7 mol.%.

[0028] In some embodiments described herein, the alkaline earth oxide further comprises at least one of SrO or BaO. The inclusion of SrO reduces the liquidus temperature of the glass composition and, as a result, improves the formability of the glass composition. For example, in some embodiments the glass composition may include SrO in an amount greater than about 0 mol.% and less than or equal to about 5 mol.%. In some of these embodiments, the glass composition may include from about 1 mol.% to about 2 mol.% SrO.

[0029] In embodiments where the glass composition includes BaO, the BaO may be present in an amount greater than about 0 mol.% and less than about 2 mol.%. In some of these embodiments, BaO may be present in the glass composition in an amount less than or equal to about 1.5 mol.% or even less than or equal to about 0.5 mol.%. However, in some other embodiments, the glass composition is free from barium and compounds of barium.

[0030] In all the embodiments of the glass compositions described herein, 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 significantly increases the chemical durability of the glass composition. In addition, it has also 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.

[0031] 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 0.5 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 0.30 mol.%.

[0032] 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 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 1.5 mol.%. For example, when the additional metal oxide is ZrO_2, the ZrO_2 may be present in an amount less than or equal to about 1.5 mol.%.

[0033] In a first exemplary embodiment, the glass composition includes from about 67 mol.% to about 75 mol.% SiO_2; from about 6 mol.% to about 10 mol.% Al_2O_3; from about 5 mol.% to about 12 mol.% alkali oxide; and from about 9 mol.% to about 15 mol.% of alkaline earth oxide. The alkali oxide comprises at least Na_2O and K_2O. The glass composition is free from boron and compounds of boron and is susceptible to ion exchange thereby facilitating chemically strengthening the glass to improve the mechanical durability.

[0034] In this first exemplary embodiment Na_2O may be present in an amount from about 6 mol.% to about 8 mol.%. The K_2O may be present in an amount less than or equal to about 0.5 mol.%. The alkali metal oxide may further comprise Li_2O in an amount from about 2 mol.% to about 3 mol.%.

[0035] In this first exemplary embodiment the alkaline earth oxide may be present in an amount from about 10 mol.% to about 14 mol.% and may comprise at least one of SrO and BaO. When the alkaline earth oxide comprises SrO, SrO may be present in an amount greater than or equal to about 1 mol.% and less than or equal to about 2 mol.%. In some of these embodiments, the glass composition is free from barium and compounds of barium. The alkaline earth oxide may also comprise MgO and CaO.

[0036] In this first exemplary embodiment the concentration of Al_2O_3 may be greater than about 7 mol. %. The glass composition may further include ZrO_2 in an amount less than or equal to about 1.5 mol.% and/or SnO_2 in an amount less than or equal to about 0.3 mol.%.

[0037] In a second exemplary embodiment, a glass composition may include from about 67 mol.% to about 75 mol.% SiO_2; from about 6 mol.% to about 10 mol.% Al_2O_3; from about 5 mol.% to about 12 mol.% alkali oxide; and from about 9 mol.% to about 15 mol.% of alkaline earth oxide. The alkaline earth oxide comprises at least one of SrO and BaO. The glass composition is free from boron and compounds of boron and is susceptible to ion exchange thereby facilitating chemically strengthening the glass to improve the mechanical durability.

[0038] In this second exemplary embodiment the alkali oxide may include Na_2O and K_2O. The Na_2O may be present in an amount from about 6 mol.% to about 8 mol.%. The K_2O may be present in an amount less than or equal to about 0.5 mol.%.

[0039] In this second exemplary embodiment, when the alkaline earth oxide comprises SrO, SrO may be present in an amount greater than or equal to about 1 mol.% and less than or equal to about 2 mol.%. In some of these embodiments, the glass composition is free from barium and compounds of barium. The alkaline earth oxide may also comprise MgO and CaO.

[0040] In this second exemplary embodiment the concentration of Al_2O_3 may be greater than about 7 mol. %. The glass composition may further include ZrO_2 in an amount less than or equal to about 1.5 mol.% and/or SnO_2 in an amount less than or equal to about 0.3 mol.%.

[0041] In the embodiments described herein the glass compositions generally have softening points of less than about 1040°C or even less than about 950°C. In some embodiments, the softening point of the glass composition is less than about 900°C. These lower softening points improve the ease of formability of the glass composition.

[0042] In the embodiments described herein the glass compositions have a CTE of less than about $70x10^{-7}K^{-1}$ or even less than about $60x10^{-7}K^{-1}$. These lower CTE values improve the survivability of the glass to thermal cycling or thermal stress conditions relative to glass compositions with higher CTEs.

[0043] As noted above, the presence of alkali oxides in the glass composition facilitates chemically strengthening the glass by ion exchange. By varying the concentration of alkali oxides in the glass, specifically the concentration of Na_2O in the glass, a wide range of compressive stresses and depth of layer values are possible for various ion-exchange processing conditions. For example, compressive stress from about 200 MPa to about 850 MPa and depth of layers from about 15 μm to about 50 μm or greater may be obtained in some glass compositions described herein after the glass composition is treated in a salt bath of 100% molten KNO_3 at a temperatures from about 400°C to about 500°C for a time period of less than about 30 hours or even less than about 20 hours.

[0044] As graphically illustrated in FIG. 1, the glass compositions described herein can be chemically strengthened by ion exchange. Exemplary depths of layer and the corresponding compressive stress are graphically depicted in FIG. 1. Also, for purposes of comparison, the depth of layer and compressive stress obtainable for Type 1b glass are also depicted. As shown in FIG. 1, the glass compositions described herein may be ion exchanged to achieve a much greater compressive stress and depth of layer than Type 1b glass.

[0045] 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.

[0046] 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 mass per surface area, specifically mg/dm^2. The DIN 12116 standard is broken into individual classes. Class S1 indicates a half weight losses of up to 0.7 mg/dm^2; Class S2 indicates a half weight losses from 0.7 mg/dm^2 up to 1.5 mg/dm^2; Class S3 indicates a half weight losses from 1.5 mg/dm^2 up to 15 mg/dm^2; and Class S4 indicates a half weight losses of more than 15 mg/dm^2.

[0047] 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 NaOH + 0.5M Na_2CO_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.

[0048] The ISO 720 standard is a measure of the resistance of the glass to degradation in distilled water. In brief, the ISO 720 standard protocol utilizes crushed grass grains which are placed in contact with 18 MΩ 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 μg 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 31 μg extracted equivalent of Na_2O; Type HGA2 is indicative of more than 31 μg and up to 62 μg extracted equivalent of Na_2O; Type HGA3 is indicative of more than 62 μg and up to 264 μg extracted equivalent of Na_2O; Type HGA4 is indicative of more than 264 μg and up to 620 μg extracted equivalent of Na_2O; and Type HGA5 is indicative of more than 620 μg and up to 1085 μg extracted equivalent of Na_2O.

[0049] The glass compositions described herein have an acid resistance of at least class S3 according to DIN 12116 with some embodiments having an acid resistance of at least class S2 or even class S1. Further, the glass compositions described herein have a base resistance according to ISO 695 of at least class A2 with some embodiments having a class A1 base resistance. The glass compositions described herein also have a DIN 12116 type HGA2 hydrolytic resistance with some embodiments having a type HGA1 hydrolytic resistance.

[0050] 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 carbonates, alkaline earth carbonates 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.

[0051] The glass compositions described herein may be shaped into various forms such as, for example, sheets, tubes or the like. However, given the chemical durability of the glass composition, the glass compositions described herein are particularly well suited for use in the formation of pharmaceutical packages for containing a pharmaceutical composition, such as liquids, powders and the like. For example, the glass compositions described herein may be used to form vials, ampoules, cartridges, syringe bodies and/or any other glass container for storing pharmaceutical compositions. Moreover, the ability to chemically strengthen the glass compositions through ion exchange can be utilized to improve the mechanical durability of such pharmaceutical packaging. Accordingly, it should be understood that, in at least one embodiment, the glass compositions are incorporated in a pharmaceutical package in order to improve the chemical durability and/or the mechanical durability of the pharmaceutical packaging.

Examples

[0052] The invention will be further clarified by the following examples.

[0053] Table 1 below contains the composition of Comparative Examples 1-4 and Inventive Examples A-C. The softening point, CTE, and chemical durability of each composition are also listed. Specifically, Comparative Examples 1-4 contained B_2O_3. Removing B_2O_3 from the glass composition to improve the chemical durability results in a corresponding undesirable increase in the softening point of the glass. In order to counteract this trend, B_2O_3 was replaced with alkali oxide, SiO_2, ZrO_2 or combinations thereof. The SiO_2 and ZrO_2 improve the chemical durability of the glass. Additions of alkali oxide lowered the softening point pf the glass by as much as 80°C. However, additions of alkali also decreased the hydrolytic durability of the glass while still meeting the ISO 720 Type HGA1 classification.

Table 1: Comparative Examples 1-4 and Inventive Examples A-C

(Mol %)	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Ex. A	Ex. B	Ex. C
SiO_2	70.8	69.9	69.3	68.3	68.6	67..7	70.8

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Al_2O_3	12.4	12.4	12.4	9	9.3	10.2	7.1
B_2O_3	1.2	0.6	1.2	0.6	0	0	0
Na_2O	0	0	0	2.5	2.5	2.5	2.5
K_2O	0	0	0	2.5	2.5	2.5	2.5
MgO	5.1	5.1	5.1	5.1	5.1	5.1	5.1
CaO	5.3	5.3	5.3	5.3	5.3	5.3	5.3
SrO	1.4	3.8	3.8	3.8	3.8	3.8	3.8
BaO	3.8	1.4	1.4	1.4	1.4	1.4	1.4
ZrO_2	0	1.5	1.5	1.5	1.5	1.5	1.5
SnO_2	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Soft pt. (°C)	1034	1031	1030	952	963	967	953
CTE (x$10^{-7}K^{-1}$)	40	37	37	48	56	56	56
DIN-12116	4.33	4.44	5.29	5.38	5.11	8.59	2.12
ISO-695	64.4	25.4	27.2	26.1	22.8	30.0	24.1
ISO-720	2.00	0.89	not tested	10.6	9.76	9.37	10.9

[0054] Table 2 shows the composition and properties of inventive Examples D-J. Specifically, the composition of inventive Examples D-J were used to assess the efficacy of further additions of alkali oxide (Na_2O, K_2O, Li_2O) on chemical durability of the glass as well as ion exchange performance. As shown in Table 2, alkali oxide additions as high as 11.5 mol.% were examined with slight increases in SiO_2 content to maintain acid durability. The softening points of these glass compositions decreased to as low as 870°C due to the increase in alkali oxide content. Moreover, neither the acid, base, nor hydrolytic resistances of these glass compositions were adversely impacted by the higher alkali level with all glasses falling into either the S2 or S3 DIN 12116 classification, the A1 ISO 695 classification, and the HGA1 ISO 720 classification.

Table 2: Compositions and Properties of Inventive Examples D-J

(Mol %)	Ex. D	Ex. E	Ex. F	Ex. H	Ex. I	Ex. J
SiO_2	70.8	72.3	72.3	71.7	71.7	71.7
Al_2O_3	7.1	7.1	7.1	7.4	7.04	7.4
Li_2O	0	0	1	0	1	1
Na_2O	2.5	2.5	2.5	10	7	10
K_2O	2.5	2.5	2.5	0.5	0.5	0.5
MgO	5.1	5.1	4.1	5.1	5.1	5.1
CaO	5.3	5.3	5.3	4.3	5.3	4.3
SrO	3.8	3.8	3.8	0.5	2	0
BaO	1.4	1.4	1.4	0.5	0	0
ZrO_2	1.5	0	0	0	0	0
SnO_2	0.3	0.3	0.3	0.3	0.3	0.3
Total	5.0	5.0	6.0 (incl.	10.5	8.5 (incl.	11.5 (incl.

Alkali			1% Li_2O)		1% Li_2O)	1% Li_2O)
Anneal pt	721	707	660	642	638	637
Soft pt. (°C)	954	942	900	873	869	869
CTE ($x10^{-7}K^{-1}$)	56.4	57.4	59.2	69.0	62.9	70.4
DIN-12116	2.73	1.74	1.66	1.73	1.49	1.50
ISO-695	20.5	41.9	52.7	69.9	57.7	45.5
ISO-720	15.6	--	13.9	15.3	11.2	17.9

[0055] The ion exchangeability of inventive Examples E-J was also investigated. Specifically, samples of the glass compositions of inventive Examples E-J were ion exchanged in a molten salt bath of 100% KNO_3 for 15 hours at temperatures of 430°C, 475°C, and 440°C. Thereafter, the surface compression and depth of layer were determined. The chemical durability of the samples was also determined following ion exchange. The results are reported in Table 3 below.

[0056] Table 3 shows that the ion exchangeability of the glass compositions is strongly dependent on the amount of alkali oxide in the composition. Compressive stress values of 200-350 MPa were reached in glass compositions with alkali oxide levels of 5 mol.% to 6 mol.%. Compressive stress values of 700-825 MPa were reached in glass compositions with alkali oxide levels of 8.5 mol.% to 11.5 mol.%. Example H had a compressive stress of 817 MPa with a depth of layer of 48 microns after ion exchange for 15 hours at 440°C for 15 hours, values which are comparable to commercially available ion exchanged damage tolerant glass.

[0057] Table 3 also shows that ion exchange treatment has minimal effect on chemical durability with the exception of the acid durability of several of the glasses with higher compressive stress values. In these instances, the glass mass lost following testing increased by a factor of 20 to 200 compared to corresponding non-ion exchanged glass compositions. While not wishing to be bound by theory, this result may be more of a manifestation of chipping of the glass edge during testing due to high compressive stress rather than actual decreased chemical resistance from ion exchange.

Table 3: Ion Exchange Properties of Examples E-J

	Ex. E	**Ex. F**	**Ex. G**	**Ex. H**	**Ex. I**	**Ex. J**
Total	5.0	5.0	6.0 (incl.	10.5	8.5 (incl.	11.5 (incl.

Alkali (mol. %)			1% Li_2O)		1% Li_2O)	1% Li_2O)
IX 430°-15hr, 100% KNO_3	233 MPa, 13 μm	214 MPa, 20 μm	325 MPa, 18 μm	750 MPa, 28 μm	705 MPa, 17 μm	800 MPa, 26 μm
IX 475°-15hr, 100% KNO_3	239 MPa, 15 μm	219 MPa, 21 μm	333 MPa, 22 μm	750 MPa, 32 μm	695 MPa, 21 μm	--
IX 440°-15hr, 100% KNO_3	--	220 MPa, 32 μm	--	817 MPa, 48 μm	--	--
DIN-12116 (IX)	2.74	2.32	30.7	52.5	538	743
Repeat	1.31	1.01	3.68	94.3	58.9	55.6
With pre-boil	1.39	1.17	2.59	80.7	42.0	57.3
ISO-695 (IX)	19.08	48.86	44.78	79.45	64.54	42.91
ISO-720 (IX)	3.07	1.84	4.46	8.93	6.41	13.66

[0058] Table 4 contains the composition and properties of several inventive examples of alkaline earth alumino-silicate glass compositions with intermediate amounts of alkali oxides (i.e., from about 5 mol.% to about 10.5 mol.%). Each of the samples exhibited an acid resistance of at least class S3 according to the DIN 12116 standard. Each of the samples also exhibited a base resistance of class A1 according to the ISO 695 standard. Test data for the ISO 720 standard was not available. The softening point of these glass compositions was in the range of 830-940°C.

[0059] Further, the glass compositions of inventive Examples K-R had compressive stress values in the range of 350-600 MPa and depth of layers up to about 50 μm.

Table 4: Composition and Properties of Examples K-R

(Mol %)	Ex. K	Ex. L	Ex. M	Ex. N	Ex. O	Ex. P	Ex. Q	Ex. R
SiO_2	72.3	72.3	72.3	72.3	71.7	72.2	71.7	71.7
Al_2O_3	7.1	7.1	7.1	7.4	7.4	7.4	7.4	7.4
Li_2O	0	0	0	0	0	0	3	1
Na_2O	2.5	4.5	5.9	7.7	7.4	10	5	7.2
K_2O	2.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5

MgO	5.1	5.1	5.1	6.8	6.5	5.1	5.1	9.1
CaO	5.3	5.3	5.3	4.3	5.5	4.3	5.3	3.3
SrO	3.8	3.8	3.8	0.5	1	0.5	2	0
BaO	1.4	1.4	0	0.5	0	0	0	0
SnO_2	0.3	0.3	0.3	0.3	0.3	0.3	0.3	.3
Strain Pt. (°C)	604	631	628	632	636	635	562	--
Anneal Pt. (°C)	653	680	678	682	686	687	609	--
Soft Pt. (°C)	887	910	913	911	916	940	834	--
CTE ($x10^{-7}K^{-1}$)	67.5	61.6	61.1	59.5	57.3	58.3	60.9	--
DIN-12116	--	1.94	1.71	1.43	1.62	--	--	--
ISO-695	--	52.3	16.6	52.7	51.6	--	--	--
ISO-720	--	--	--	--	--	--	--	--
IX 440°-15hr, 100% KNO_3	--	600 MPa, 25 μm	610 MPa 25 μm	522 MPa 15 μm	--	--	730 MPa, 13 μm	--
IX 475°-15hr, 100% KNO_3	--	590 MPa, 37 μm	600 MPa 40 μm	520 MPa 22 μm	424 MPa 12 μm	--	--	--
IX 490°-15hr, 100% KNO_3	--	497 MPa, 43 μm	521 MPa 49 μm	442 MPa 30 μm	375 MPa 16 μm	--	--	--

[0060] It should now be understood that the glass compositions described herein exhibit chemical durability as well as mechanical durability following ion exchange. These properties make the glass compositions well suited for use in various applications including, without limitation, pharmaceutical packaging materials.

[0061] 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.

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The claims defining the invention are as follows:

1. A glass composition comprising:

from 67 mol.% to about 75 mol.% SiO_2;

from about 6 mol.% to about 10 mol.% Al_2O_3;

from about 5 mol.% to about 12 mol.% alkali oxide, wherein the alkali oxide comprises Na_2O and K_2O and the K_2O is present in an amount less than or equal to 0.5 mol.%; and

from about 9 mol.% to about 15 mol.% of alkaline earth oxide,

the glass composition is susceptible to strengthening by ion-exchange, free from boron and compounds of boron, and has a CTE less than 60×10^{-7}/K from room temperature to 300°C.

2. A glass composition comprising:

from 67 mol.% to about 75 mol.% SiO_2;

from about 6 mol.% to about 10 mol.% Al_2O_3;

from about 5 mol.% to about 12 mol.% alkali oxide, wherein the alkali oxide comprises K_2O in an amount less than or equal to about 0.5 mol.%;

from about 9 mol.% to about 15 mol.% of alkaline earth oxide, wherein the alkaline earth oxide comprises at least one of SrO and BaO, wherein:

the glass composition is free from boron and compounds of boron;

the glass composition has a CTE less than 60×10^{-7}/K from room temperature to 300°C; and

the glass composition is ion exchangeable to a depth of layer greater than or equal to about 15 μm and less than or equal to 50 μm with a corresponding compressive stress greater than or equal to about 200 MPa and less than or equal to 800 MPa.

3. The glass composition of claim 1, wherein the alkaline earth oxide comprises at least one of SrO and BaO.

4. The glass composition of claim 2 or claim 3, wherein the alkaline earth oxide comprises SrO in an amount greater than or equal to about 1 mol.% and less than or equal to about 2 mol.%.

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5. The glass composition of any one of claims 1 to 4, wherein a concentration of Al_2O_3 is greater than about 7 mol.%.

6. The glass composition of any one of claims 1 to 4, wherein the alkali oxide further comprises Li_2O in an amount from about 1 mol.% to about 3 mol.%.

7. The glass composition of any one of claims 1 to 5, wherein the Na_2O is present in an amount from about 3.5 mol.% to about 8 mol.%.

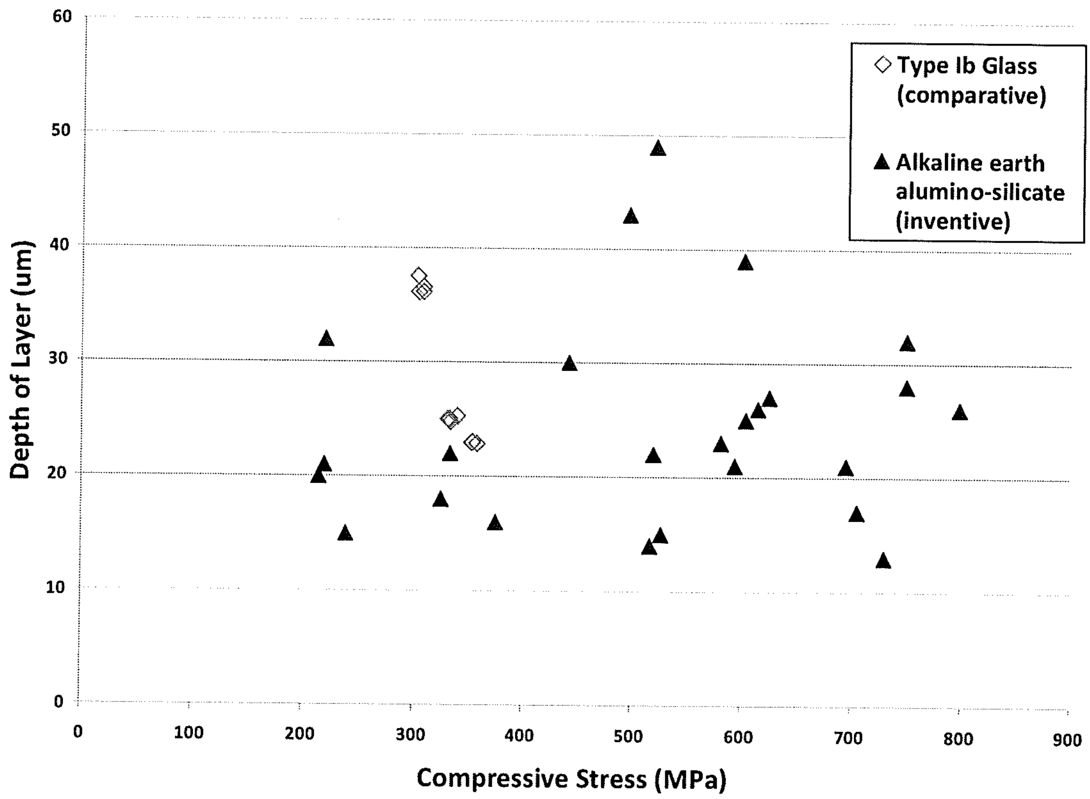
8. The glass composition of any one of claims 1 to 7, wherein the alkaline earth oxide is present in an amount from about 10 mol.% to about 14 mol.%.

9. The glass composition of any one of claims 1 to 8, wherein the glass composition has at least a class S3 acid resistance according to DIN 12116.

10. The glass composition of any one of claims 1 to 9, wherein the glass composition has a class A1 base resistance according to ISO 695.

11. The glass composition of any one of claims 1 to 10, wherein the glass composition has a type HGA1 hydrolytic resistance according to ISO 720.

12. The glass composition of any one of claims 3 to 11, wherein the alkaline earth oxide further comprises MgO and CaO.



Type Ib Glass
(comparative)
Alkaline earth
alumino-silicate
(inventive)
Depth of Layer (um)
Compressive Stress (MPa)
0
10
20
30
40
50
60
0
100
200
300
400
500
600
700
800
900

FIG. 1