CLAIMS

What is claimed is:

1. A glass composition comprising:

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, wherein the alkali oxide comprises Na_2O in an amount greater than about 8 mol.%, a ratio of Y:X is greater than 1, and the glass composition is free of boron and compounds of boron.

2. A glass composition comprising:

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;

Y mol.% alkali oxide, wherein the alkali oxide comprises Na_2O in an amount greater than about 8 mol.%; and

B_2O_3, wherein a ratio (B_2O_3 (mol.%)/(Y mol.% – X mol.%) is greater than 0 and less than 0.3, and a ratio of Y:X is greater than 1.

3. A glass composition comprising:

from about 70 mol.% to about 80 mol.% SiO_2;

from about 3 mol.% to about 13 mol.% alkaline earth oxide, wherein the alkaline earth oxide comprises CaO in an amount greater than or equal to about 0.1 mol.% and less than or equal to about 1.0 mol.%;

X mol.% Al_2O_3, wherein X is greater than or equal to about 2 mol.% and less than or equal to about 10 mol.%; and

Y mol.% alkali oxide, wherein the alkali oxide comprises from about 0.01 mol.% to about 1.0 mol.% K_2O and a ratio of Y:X is greater than 1, and the glass composition is free of boron and compounds of boron.

4. A glass composition comprising:

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, wherein the alkali oxide comprises Na_2O in an amount greater than about 8 mol.%, wherein:

a ratio of a concentration of B_2O_3 (mol.%) in the glass composition to (Y mol.% – X mol.%) is less than 0.3; and

a ratio of Y:X is greater than 1.

5. A glass composition comprising:

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, 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 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 is greater than 1, and the glass composition is free of boron and compounds of boron.

6. A glass composition comprising:

SiO_2 in a concentration greater than about 70 mol.%; and

Y mol.% alkali oxide, wherein the alkali oxide comprises Na_2O in an amount greater than about 8 mol.%, wherein the glass composition is free of boron and compounds of boron.

7. A glass composition comprising:

greater than about 68 mol.% SiO_2;

X mol.% Al_2O_3;

Y mol% alkali oxide, wherein the alkali oxide comprises Na_2O in an amount greater than about 8 mol%; and

B_2O_3, wherein a ratio (B_2O_3 (mol.%)/(Y mol.% – X mol.%) is greater than 0 and less than 0.3.

8. The glass composition of any of claims 1-4, 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.%.

9. The glass composition of any of claims 6-7, further comprising from about 3 mol.% to about 13 mol.% alkaline earth oxide.

10. The glass composition of claim 9, wherein the alkaline earth oxide comprises MgO and CaO, wherein:

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.

11. The glass composition of any of claims 1-5, 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.

12. The glass composition of any of claims 1-2 and 4-5, wherein the alkaline earth oxide comprises from about 0.1 mol.% to less than or equal to about 1.0 mol.% CaO.

13. The glass composition of any of claims 1-5, wherein the alkaline earth oxide comprises from about 3 mol.% to about 7 mol.% MgO.

14. The glass composition of any of claims 1, 2, 4, and 7 wherein X is greater than or equal to about 2 mol.% and less than or equal to about 10 mol.%.

15. The glass composition of any of claims 1-4 and 6-7, 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.

16. The glass composition of claim 6 further comprising X mol.% Al_2O_3, wherein a ratio of Y:X is greater than 1.

17. The glass composition of claim 16, wherein X is greater than or equal to about 2 mol.% and less than or equal to about 10 mol.%.

18. The glass composition of claim 7, wherein a ratio of Y:X is greater than 1.

19. The glass composition of any of claims 1-5, 16 and 18, wherein the ratio of Y:X is less than or equal to 2.

20. The glass composition of any of claims 1-5, 16 and 18, wherein the ratio of Y:X is greater than or equal to 1.3 and less than or equal to 2.0.

21. The glass composition of any of claims 1-7 wherein the glass composition is free of phosphorous and compounds of phosphorous.

22. The glass composition of any of claims 1-2 and 4-7, 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.%.

23. The glass composition of any of claims 2, 4, and 7, wherein an amount of SiO_2 is greater than or equal to about 70 mol.%.

24. The glass composition of any of claims 2, 4, and 7, wherein the ratio (B_2O_3 (mol.%)/(Y mol.% – X mol.%) is less than 0.2.

25. The glass composition of any of claims 2, 4, and 7, wherein an amount of B_2O_3 is less than or equal to about 4.0 mol.%.

26. The glass composition of claim 25, wherein the amount of B_2O_3 is greater than or equal to about 0.01 mol.%.

27. The glass composition of claim 4, wherein the glass composition is free from boron and compounds of boron.

28. The glass composition of any of claims 1-4 and 6-7, wherein a concentration of SiO_2 is greater than or equal to about 72 mol.%.

29. The glass composition of any of claims 1-7, wherein a concentration of SiO_2 is greater than or equal to about 73 mol.%.

30. A glass article formed from the glass composition of any of claims 1-7.

31. The glass article of claim 30, wherein the glass article has a type HGB1 hydrolytic resistance according to ISO 719.

32. The glass article of claim 30, wherein the glass article has a type HGA1 hydrolytic resistance according to ISO 720 after ion exchange strengthening.

33. The glass article of claim 30, wherein the glass article has a type HGA1 hydrolytic resistance according to ISO 720 before and after ion exchange strengthening.

34. The glass article of claim 31, wherein the glass article has at least a class S3 acid resistance according to DIN 12116.

35. The glass article of claim 31, wherein the glass article has at least a class A2 base resistance according to ISO 695.

36. The glass article of claim 31, wherein the glass article is a pharmaceutical package.

37. The glass article of claim 31, wherein the glass article is ion exchange strengthened.

38. The glass article of claim 31 further comprising a compressive stress layer with a depth of layer greater than or equal to 10 μm and a surface compressive stress greater than or equal to 250 MPa.

39. A glass article comprising:

a type HGB1 hydrolytic resistance according to ISO 719; and

a threshold diffusivity of greater than 16 $\mu m^2/hr$ at a temperature less than or equal to 450°C.

40. The glass article of claim 39, wherein the glass article has a type HGA1 hydrolytic resistance according to ISO 720 after ion exchange strengthening.

41. The glass article of claim 39 further comprising a compressive stress layer with a depth of layer greater than 25 μm.

42. The glass article of claim 41, 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.

43. The glass article of claim 39 further comprising a surface compressive stress greater than or equal to 350 MPa.

44. The glass article of claim 43, 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.

45. The glass article of claim 39, wherein the glass article is a pharmaceutical package.

46. A glass article comprising:

a type HGB1 hydrolytic resistance according to ISO 719;

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, 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.

47. The glass article of claim 46, wherein the glass article has a type HGA1 hydrolytic resistance according to ISO 720 after ion exchange strengthening.

48. The glass article of claim 46, wherein the glass article has a threshold diffusivity of greater than 16 μm^2/hr at a temperature of less than or equal to 450°C.

49. The glass article of claim 46, wherein the glass article is a pharmaceutical package.

50. A glass article comprising:
a type HGB1 hydrolytic resistance according to ISO 719;
greater than about 8 mol.% Na_2O; and
less than about 4 mol.% B_2O_3.

51. The glass article of claim 50 further comprising:
X mol.% Al_2O_3;
Y mol.% alkali oxide, wherein a ratio (B_2O_3 (mol.%)/(Y mol.% – X mol.%) is greater than 0 and less than 0.3.

52. The glass article of claim 50 further comprising a compressive stress layer having a surface compressive stress greater than or equal to about 250 MPa.

53. The glass article of claim 50, wherein the glass article has at least a class S3 acid resistance according to DIN 12116.

54. The glass article of claim 50, wherein the glass article has at least a class A2 base resistance according to ISO 695.

55. The glass article of claim 50, wherein the glass article has a type HGA1 hydrolytic resistance according to ISO 720.

56. A glass pharmaceutical package comprising:
SiO_2 in an amount greater than about 70 mol.%;
X mol.% Al_2O_3;
Y mol.% alkali oxide, wherein the alkali oxide comprises Na_2O in an amount greater than about 8 mol.%; and

the loss of active drug product leading to increased costs. 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 package is to thermally temper the glass package. 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, pharmaceutical glass packages typically have complex geometries (vial, tubular, ampoule, etc.), thin walls (~1-1.5 mm), and are produced from low expansion glasses ($30\text{-}55 \times 10^{-7} K^{-1}$) making glass pharmaceutical packages 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 compositions which are chemically durable and susceptible to chemical strengthening by ion exchange for use in glass pharmaceutical packages, and similar applications.

SUMMARY

[0008] In one aspect, there is provided a glass composition comprising: SiO_2 in a concentration greater than 74 mol.%; alkaline earth oxide comprising MgO and CaO, wherein CaO is present in an amount greater than or equal to 0.1 mol.% and less than or equal to 1.0 mol.%, and a ratio (CaO (mol.%)/(CaO (mol.%)+MgO (mol.%))) is less than or equal to 0.5; and Y mol.% alkali oxide, wherein the alkali oxide comprises Na_2O in an amount greater than 8 mol.%, wherein the glass composition is free of boron and compounds of boron.

[0008a] According to one ~~embodiment~~example, 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.

[0009] According to another ~~embodiment~~example, 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 (mol.%)/(Y mol.% – X mol.%) may be greater than 0 and less than 0.3.

[0010] In yet another example~~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.

[0011] In still another example~~embodiment~~, a glass pharmaceutical package 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 pharmaceutical package to (Y mol.% – X mol.%) may be less than 0.3. The glass pharmaceutical package may also have a type HGB1 hydrolytic resistance according to ISO 719.

[0012] In another example~~embodiment~~, 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.

[0013] In yet another example~~embodiment~~, 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.

[0014] In still another example~~embodiment~~, 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 (mol.%)/(Y mol.% – X mol.%) may be greater than 0 and less than 0.3, and a ratio of Y:X may be greater than 1.

[0015] In another example~~embodiment~~, 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.

[0016] In yet another example~~embodiment~~, 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.

[0017] In another example~~embodiment~~, 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°C.

[0018] In yet another example~~embodiment~~, 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.

[0019] 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 example ~~embodiments~~ described herein, including the detailed description which follows, the claims, as well as the appended drawings.

[0020] It is to be understood that both the foregoing general description and the following detailed description describe various example ~~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 example~~embodiments~~, and are incorporated into and constitute a part of this specification. The

drawings illustrate the various ~~embodiments~~ examples described herein, and together with the description serve to explain the principles and operations of the claimed subject matter.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021] 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;

[0022] 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;

[0023] 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;

[0024] FIG. 4 graphically depicts diffusivity D (y-axis) as a function of the ratio (CaO/(CaO+MgO)) (x-axis) for inventive and comparative glass compositions;

[0025] FIG. 5 graphically depicts the maximum compressive stress (y-axis) as a function of the ratio (CaO/(CaO+MgO)) (x-axis) for inventive and comparative glass compositions;

[0026] FIG. 6 graphically depicts diffusivity D (y-axis) as a function of the ratio (B_2O_3/(R_2O-Al_2O_3)) (x-axis) for inventive and comparative glass compositions; and

[0027] FIG. 7 graphically depicts the hydrolytic resistance as determined from the ISO 720 standard (y-axis) as a function of the ratio (B_2O_3/(R_2O-Al_2O_3)) (x-axis) for inventive and comparative glass compositions.

DETAILED DESCRIPTION

[0028] 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 may generally comprise silica (SiO_2), alumina (Al_2O_3), alkaline earth oxides (such as

CLAIMS

1. A glass composition comprising:

SiO_2 in a concentration greater than 74 mol.%;

alkaline earth oxide comprising MgO and CaO, wherein CaO is present in an amount greater than or equal to 0.1 mol.% and less than or equal to 1.0 mol.%, and a ratio (CaO (mol.%)/(CaO (mol.%)+MgO (mol.%))) is less than or equal to 0.5; and

Y mol.% alkali oxide, wherein the alkali oxide comprises Na_2O in an amount greater than 8 mol.%, wherein the glass composition is free of boron and compounds of boron.

2. The glass composition of claim 1 wherein the concentration of SiO_2 is less than or equal to 80 mol.%.

3. The glass composition of claim 1 further comprising X mol.% Al_2O_3, wherein a ratio of Y:X is greater than 1 and less than or equal to 2.

4. The glass composition of claim 3, wherein X is greater than or equal to 2 mol.% and less than or equal to 10 mol.%.

5. The glass composition of claim 1, wherein the alkaline earth oxide is present in an amount from 3 mol.% to 13 mol.%.

6. The glass composition of claim 3, wherein the ratio of Y:X is greater than or equal 1.3 and less than or equal to 2.

7. A glass composition according to claim 1 comprising:

from 74 mol.% to 78 mol.% SiO_2;

from 4 mol.% to 8 mol.% alkaline earth oxide;

X mol.% Al_2O_3, wherein X is greater than or equal to 2 mol.% and less than or equal to 10 mol.%; and

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 a ratio of Y:X is greater than 1.

8. The glass composition of claim 1 or claim 7, wherein the alkaline earth oxide comprises from about 3 mol.% to about 7 mol.% MgO.

9. The glass composition of claim 1, comprising:

from 74 mol.% to 78 mol.% SiO_2;

from 4 mol.% to 8 mol.% alkaline earth oxide;

X mol.% Al_2O_3, wherein X is greater than or equal to 4 mol.% and less than or equal to 8 mol.%; and

Y mol.% alkali oxide, wherein the alkali oxide comprises Na_2O in an amount greater than or equal to 9 mol.% and less than or equal to 15 mol.%, a ratio of Y:X is greater than 1, and the glass composition is free of boron and compounds of boron, wherein the glass composition has a type HGA1 hydrolytic resistance according to ISO 720.

10. The glass composition of claim 1 or claim 9, wherein the glass composition has a threshold diffusivity greater than 16 $\mu m^2/hr$ at a temperature less than or equal to 450°C.