INSTRUCTIONS

(a) If Convention application insert "Convention"

Beall 52-4 (a)

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(b) Delete one

APPLICATION FOR A (b) STANDARD/~~PETTY~~ PATENT

(c) Insert FULL name(s) of applicant(s)

I/We (c) CORNING INCORPORATED

620919

(d) Insert FULL address(es) of applicant(s)

of (d) Corning, New York 14831,
United States of America

(e) Delete one

hereby apply for the grant of a (e) Standard/~~Petty~~ Patent for an invention entitled

(f) Insert TITLE of invention

(f) ZINC-CONTAINING PHOSPHATE GLASSES

(g) Insert "complete" or "provisional" or "petty patent"

which is described in the accompanying (g) complete specification.

(Note: The following applies only to Convention applications)

Details of basic application(s)

(h) Insert number, country and filing date for the/or each basic application

	Application No.	Country	Filing Date
(h)	258,675	United States of America	17 October 1988

Address for Service: PHILLIPS ORMONDE AND FITZPATRICK
Patent and Trade Mark Attorneys
367 Collins Street
Melbourne, Australia 3000

(i) Insert date of signing

Dated (i) July 10, 1989

(j) Signature of applicant(s) (For body corporate see headnote*)

(j) Alfred L. Michaelsen
Vice President

(k) Corporate seal if any

(k)

Note: No legalization or other witness required

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Beall 52-4

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DECLARATION FOR A PATENT APPLICATION

▼ **INSTRUCTIONS**
(a) Insert "Convention" if applicable
(b) Insert FULL name(s) of applicant(s)

In support of the (a) convention application made by
(b)
CORNING INCORPORATED

(c) Insert "of addition" if applicable
(d) Insert TITLE of invention

(hereinafter called "applicant(s) for a patent (c) for an invention entitled (d)

ZINC-CONTAINING PHOSPHATE GLASSES

(e) Insert FULL name(s) AND address(es) of declarant(s) (See headnote*)

I/We (e) ALFRED L. MICHAELSEN, Vice President of Corning Incorporated, Corning, New York 14831, United States of America

do solemnly and sincerely declare as follows:

~~I am/We are the applicant(s).~~

(or, in the case of an application by a body corporate)

1. I am/We are authorized to make this declaration on behalf of the applicant(s).

~~2. I am/We are the actual inventor(s) of the invention.~~

(or, where the applicant(s) is/are not the actual inventor(s))

(f) Insert FULL name(s) AND address(es) of actual inventor(s)

2. (f)
GEORGE HALSEY BEALL of 106 Woodland Drive, Big Flats, New York, United States of America and
CANDACE JO QUINN of Thurber Road, Corning, New York, United States of America

is/are the actual inventor(s) of the invention and the facts upon which the applicant(s) is/are entitled to make the application are as follows:

(g) Recite how applicant(s) derive(s) title from actual inventor(s) (See headnote**)

(g)
Applicant is the assignee of the invention from the actual inventors

(Note: *Paragraphs 3 and 4 apply* **only** *to Convention applications)*

(h) Insert country, filing date, and basic applicant(s) for the/or EACH basic application

3. The basic application(s) for patent or similar protection on which the application is based is/are identified by **country, filing date, and basic applicant(s)** as follows:

(h)
United States of America, 17 October 1988
George Halsey Beall and Candace Jo Quinn

4. The basic application(s) referred to in paragraph 3 hereof was/were the first application(s) made in a Convention country in respect of the invention the subject of the application.

(k) Insert PLACE of signing

(l) Insert DATE of signing

(m) Signature(s) of declarant(s)

Note: No legalization or other witness required

Declared at (k) Corning, New York

Dated (l) July 10, 1989

(m) CORNING INCORPORATED

Alfred L. Michaelsen

Alfred L. Michaelsen
Vice President

To: The Commissioner of Patents

P18/7/78

PHILLIPS ORMONDE & FITZPATRICK
Patent and Trade Mark Attorneys
367 Collins Street
Melbourne, Australia

(12) PATENT ABRIDGMENT (11) Document No. AU-B-42731/89
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 620919

(54) Title
ZINC-CONTAINING PHOSPHATE GLASSES

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(56) Prior Art Documents
US 4544974
US 4439530
US 4248732

(57) Claim

1. A glass exhibiting a transition temperature below 450°C, a working temperature below 500°C, and excellent resistance to attack by water and mild aqueous alkaline solutions, said glass comprising, expressed in terms of mole percent on the oxide basis, at least 65% total of 12-55% ZnO, 28-40% P_2O_5, and 10-35% R_2O, wherein R_2O consists of at least two alkali metal oxides in the indicated proportions selected from the group consisting of 0-25% Li_2O, 0-25% Na_2O, and 0-25% K_2O, and up to 35% total of optional ingredients in the indicated proportions selected from the group consisting of 0-6% Al_2O_3, 0-8% B_2O_3, 0-8% $Al_2O_3+B_2O_3$, 0-15% Cu_2O, 0-5% F, 0-35% PbO, 0-35% SnO, 0-35% PbO+SnO, 0-5% ZrO_2, 0-4% SiO_2, and 0-15% MgO+CaO+SrO+BaO+MnO, consisting of 0-10% MgO, 0-10% CaO, 0-10% SrO, 0-12% BaO, and 0-10% MnO.

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COMPLETE SPECIFICATION 620919
(ORIGINAL)

Class Int. Class

Application Number:
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Complete Specification Lodged:
Accepted:
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Priority

Related Art:

Applicant(s):

Corning Incorporated
Corning, New York, 14831, UNITED STATES OF AMERICA

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367 Collins Street
Melbourne 3000 AUSTRALIA

Complete Specification for the invention entitled:

ZINC-CONTAINING PHOSPHATE GLASSES

Our Ref : 142195
POF Code: 103486/103486

The following statement is a full description of this invention, including the best method of performing it known to applicant(s):

6006

ZINC-CONTAINING PHOSPHATE GLASSES

~~Related Applications~~

U. S. Application Serial No. , filed concurrently herewith by us under the title R_2O-Al_2O_3/B_2O_3-P_2O_5 GLASSES, discloses the formulation of glasses consisting essentially, in mole percent, of 4-10% $Al_2O_3+B_2O_3$, consisting of 0-7% Al_2O_3 and 0-10% B_2O_3, 10-45% Na_2O+Li_2O, consisting of 10-30% Na_2O and 0-30% Li_2O, 10-30% Li_2O+Cu_2O, consisting of 0-20% Cu_2O and 0-30% Li_2O, and 44-58% P_2O_5.

U. S. Application Serial No. , filed concurrently by G. H. Beall, J. E. Pierson, and C. J. Quinn under the title ALKALI ZINC ALUMINOPHOSPHATE GLASS-CERAMICS, discloses the production of glass-ceramics consisting essentially, in mole percent, of 5-25% R_2O, wherein R_2O consists of 5-25% Li_2O, 0-15% Na_2O, and 0-15% K_2O, 35-50% ~~ZnO, 0.75-6% Al_2O_3, and 29-37% P_2O_5~~.

Background of the Invention

Research has been continuous to develop inorganic glasses exhibiting low transformation or transition temperatures (Tg), thereby making it possible to conduct melting and forming operations at low temperatures. Inasmuch as glass compositions wherein silica comprises the primary network or glass forming component customarily manifest transition temperatures considerably in excess of 450°C with forming temperatures greater than 800°C, the desire

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for glass compositions displaying low transition temperatures has typically resulted in the use of B_2O_3 and/or P_2O_5 as the principal network forming constituent. U. S. Patent No. 3,732,181 discloses three general areas of glass compositions, wherein P_2O_5 is the principal glass former, which exhibit transition temperatures within the interval of 100°-400°C:

(a) 20-80 mole % PbO + P_2O_5 ≥95 mole %

(b) 5-60 mole % PbO + 5-35 mole % R_2O + up to 85 mole % P_2O_5 ≥95 mole %

(c) 5-30 mole % PbO + 5-30 mole % R_2O + 5-20 mole % B_2O_3 + 15-85 mole % P_2O_5 ≥95 mole %.

It is stated that ZnO may replace part or all of the PbO.

Unfortunately, phosphate-based glasses typically exhibit poorer chemical durability than silica-based glasses, and that characteristic commonly becomes more pronounced as the transition temperature of the glass becomes lower. Thus, the known low melting phosphate glasses are frequently readily attacked by boiling water and, in extreme instances, manifest hygroscopic behavior. As conventionally defined, the transition temperature of a glass is that temperature at which increases in specific heat and thermal expansion coefficient take place which are accompanied by a sharp drop in viscosity.

Accordingly, the primary objective of the present invention was to develop glasses exhibiting transition temperatures below 450°C, preferably below 350°C, with working temperatures (temperatures at which the glass demonstrates a viscosity of about 10^4-10^7 poises) below 500°C, preferably between about 350°-450°C, which glasses display exceptional chemical durability when contacted with boiling water and mild aqueous alkaline solutions.

Summary of the Invention

That objective can be achieved in glasses having compositions within a specifically-defined region of the

R_2O-ZnO-P_2O_5 system, wherein R_2O consists of Li_2O, Na_2O, and/or K_2O, and wherein PbO and/or SnO can replace a portion of the ZnO content. Hence, because PbO and/or SnO can be substituted for ZnO in amounts up to 35 mole percent, the broad composition area operable in the present invention consists essentially, expressed in terms of mole percent on the oxide basis, of 10-35% R_2O, wherein R_2O consists of at least two alkali metal oxides in the indicated proportions of 0-25% Li_2O, 0-25% Na_2O, and 0-25% K_2O, 12-55% ZnO, (preferably 23-55% ZnO) 28-40% P_2O_5, and, optionally, up to 35% RO, wherein RO consists of 0-35% PbO and 0-35% SnO. The inclusion of at least two alkali metal oxides has been found necessary since laboratory experience has indicated that the presence of Li_2O alone hazards devitrification in the glass, Na_2O alone renders the glass insufficiently durable or too difficult to melt, and K_2O alone raises the Tg of the glass too high.

Additions of Al_2O_3 in amounts ranging about 0.75-6% and/or B_2O_3 at levels about 1-8% are particularly useful in enhancing the chemical durability of the glass and/or improving glass stability, the total of those additions not exceeding 8%. Consequently, the preferred inventive glasses will contain one or both of those components.

CaO, MgO, and MnO may be included in individual concentrations up to 10%, with the total of those constituents not exceeding 10%. Cu_2O may be present up to 15%. MnO and Cu_2O exhibit the capability of reducing the Tg of the glass while maintaining good chemical durability therein. Additions of other compatible oxides and fluoride (F_2) can be tolerated in amounts not exceeding about 5%. ZrO_2 is particularly useful in imparting a uniform white opal coloration to the glasses in amounts of about 1-5%.

The sum of all optional components will not total more than about 40%.

In the preferred compositions the sum of R_2O + Al_2O_3 and/or B_2O_3 + ZnO + P_2O_5 with, optionally, PbO and/or SnO will total at least 85%. The most preferred glasses

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consist essentially of 12-25% R_2O, wherein R_2O consists of at least two alkali metal oxides in the indicated proportions 3-12% Li_2O, 4-13% Na_2O, and 0-12% K_2O, 30-49% ZnO, 0-10% SnO, 1-3.5% Al_2O_3, and 30-36% P_2O_5 with the proviso that, if present, the sum of CaO + MgO + F will not exceed 5%.

Whereas the complete conversion of composition ranges expressed in terms of mole percent to ranges expressed in terms of weight percent is not mathematically possible, the following intervals comprise approximate values of the above ranges in terms of weight percent. Thus, the broad composition area consists essentially of 5-25% R_2O, wherein R_2O consists of at least two alkali metal oxides in the indicated proportions of 0-10% Li_2O, 0-15% Na_2O, and 0-20% K_2O, 6-45% ZnO, 30-57% P_2O_5, and optionally, up to 55% RO, wherein RO consists of 0-50% PbO and 0-40% SnO. In the preferred compositions 0.75-6% Al_2O_3 and/or 1-6% B_2O_3 will be included, the total of those components not exceeding about 6%.

Prior Art

U. S. Patent No. 3,215,543 describes the production of articles composed of mica particles dispersed in a glassy matrix, the glassy matrix consisting essentially, in mole percent, of 6-20% RO, wherein RO consists of CaO, MgO, and/or ZnO, 22-42.5% R_2O, wherein R_2O consists of the alkali metal oxides, 6 to $(16+\frac{d}{6})$% Al_2O_3, and $(36-\frac{d}{3})$ to (56-d)% P_2O_5, where d comprises the percentage of RO. The Al_2O_3 content is in excess of that which can be tolerated in the present inventive compositions.

U. S. Patent No. 3,407,091 discloses the preparation of sealing glasses consisting essentially, in weight percent, of 4-27% Na_2O and/or K_2O, 4-30% ZnO, 2-10% Al_2O_3, and 60-67% P_2O_5. The P_2O_5 concentration is greater than that which is permissible in the present inventive glasses.

U. S. Patent No. 3,481,749 sets forth glasses suitable as lubricants for use, for example, in the extrusion of metallic bodies at elevated temperatures. That application requires a glass readily attacked by water to permit easy removal from the body by washing after use. The glasses consisted essentially, in molar percent, of 9-33% alkali metal oxide, 16-20% BaO, CaO, MgO, PbO, and/or ZnO, 10-20% Al_2O_3, and 29-61% P_2O_5. The Al_2O_3 level is far above that found operable in the present invention. Moreover, the poor chemical durability of the glasses would render them useless in the applications envisioned for the present inventive glasses.

U. S. Patent No. 3,732,181 was reviewed in some detail above. Al_2O_3 is nowhere mentioned as a glass component and all of the working examples have compositions quite far removed from the ranges of the present invention.

U. S. Patent No. 3,885,973 teaches the preparation of glasses having compositions consisting essentially, in mole percent, of 5-25% Li_2O, 5-30% ZnO, 58-76% P_2O_5, and 0-10% alkaline earth oxides, and may contain up to 5% by weight water. There is no requirement for the presence of at least two alkali metal oxides and no working example contained two, and the concentrations of P_2O_5 far exceed those found operable in the instant inventive glasses.

U. S. Patent No. 3,926,649 describes the production of glasses having compositions consisting essentially, in mole percent, of 72.5-77.5% P_2O_5+B_2O_3 and 22.5-27.5% alkali metal oxides, alkaline earth metal oxides, and ZnO, and may contain up to 5% by weight water. There is no requirement for the inclusion of at least two alkali metal oxides and in all of the working examples the P_2O_5 content is much higher than can be tolerated in glasses of the present invention.

U. S. Patent No. 3,935,018 discloses the formulation of glasses having compositions consisting essentially, in mole percent, of 1.2-3.5% B_2O_3, 50-72% P_2O_5, 0-30% PbO, 0-5% transition metal oxides, and the remainder alkali

metal oxides, alkaline earth metal oxides, and/or ZnO, and may contain up to 5% by weight water. No working example contained ZnO and the P_2O_5 level is greater than that found operable in the present inventive glasses.

U. S. Patent No. 3,979,322 sets forth glasses suitable for laser applications consisting essentially, in mole percent, of 1-30% alkali metal oxides, 20-45% group II metal oxides, 0.1-25% Nd_2O_3, 35-49% P_2O_5, and 0-27% Al_2O_3, B_2O_3, Nb_2O_5, and/or PbO. There is no requirement that at least two alkali metal oxides be present and one of the working examples contained two. Moreover, the P_2O_5 contents and, where present, the alkaline earth metal oxides concentrations in the working examples were substantially in excess of those delimited in the glasses of the instant invention.

U. S. Patent No. 4,026,714 discusses the production of glasses exhibiting anti-misting properties, the phenomenon of anti-misting being the result of the glasses being slightly hygroscopic. Such glasses would not be suitable for the purposes of the present invention. The glasses consisted essentially, in mole percent, of 4-30% alkali metal oxides, alkaline earth metal oxides, or ZnO, 1-12% PbO, 3.5-12% B_2O_3 and/or SiO_2 and/or Al_2O_3, and 52-72% P_2O_5. The P_2O_5 content is far in excess of that which is operable in the present invention.

U. S. Patent No. 4,060,422 relates to sealing glasses for glass lasers consisting essentially, in mole percent, of 4-12% Li_2O, 5-25% PbO, 15-35% ZnO, 1-4% Al_2O_3, 2-10% V_2O_5, and 45-65% P_2O_5. The P_2O_5 level is higher than is suitable in the present inventive glasses.

U. S. Patent No. 4,229,220 is concerned with glasses useful in coating glass laser discs consisting essentially, in mole percent of 0-20% Li_2O, 0-17% Na_2O, 8-20% Li_2O+Na_2O, 7-28% CuO, 4-10% Al_2O_3, 51-59% P_2O_5, 0-8% B_2O_3, 0-2% ZnO, 0-15% BaO, and 0-13% V_2O_5. The concentration of P_2O_5 exceeds that found operable in the present inventive glasses.

U. S. Patent No. 4,239,645 is drawn to laser glasses consisting essentially, in mole percent, of 10-25% R_2O, wherein R_2O consists of 0-25% Li_2O, 0-25% Na_2O, and 0-8% K_2O, 5-15% RO, wherein RO consists of 0-15% BaO, 0-15% CaO, 0-15% MgO, 0-15% SrO, and 0-15% ZnO, 1-15% Al_2O_3, 55-70% P_2O_5, 0.01-5% Nd_2O_3, 0-5% Y_2O_3, 0-5% La_2O_3, 0-5% GeO_2, 0-5% CeO_2, 0-3% Nb_2O_5, 0-3% MnO_2, 0-2% Ta_2O_5, and 0-1% Sb_2O_3. The P_2O_5 content is greater than that specified in the present invention.

U. S. Patent No. 4,248,732 refers to laser glasses consisting essentially, in mole percent, of 5-40% alkali metal oxides, 5-30% RO, wherein RO is at least one oxide selected from the group BaO, BeO, CaO, MgO, SrO, and ZnO, 0.01-15% R_2O_3, where R_2O_3 is at least one oxide selected from the group Al_2O_3, B_2O_3, Er_2O_3, La_2O_3, Tm_2O_3, and Y_2O_3, 0.01-7% Nd_2O_3, 35-65% P_2O_5, and 0.1-10% by weight of a solarization inhibiting oxide selected from the group of CeO_2, Nb_2O_5, Sb_2O_3, SiO_2, and TiO_2. Such ranges and the components making up those ranges are far broader and more diverse than can be tolerated in the present inventive glasses. Even excluding the required inclusion of Nd_2O_3 and the solarization inhibitor, none of the 29 working examples provided in the patent had a composition coming within the ranges delimited in the present invention.

U. S. Patent No. 4,391,915 records glasses from which optical components can be pressed consisting essentially, in weight percent, of 5-20% K_2O, 0-3% Li_2O, 8-15% BaO, 0-6% MgO, 0-18% PbO, 4.5-9% ZnO, 3.5-9% Al_2O_3, 0-3% B_2O_3, 0-1% SiO_2, 0-2% TiO_2, 45-55% P_2O_5. The content of BaO exceeds that which can be tolerated in the present inventive glasses. Moreover, the level of P_2O_5 in mole percent in all of the working examples provided in the patent was higher than the maximum permitted in the present inventive glasses.

U. S. Patent No. 4,439,530 reports optical glasses basically consisting essentially, in weight percent, of 3-30% R_2O, wherein R_2O consists of 0-30% Na_2O+0-30% K_2O,

8-65% PbO, 1-45% Ta_2O_5, and 18-38% P_2O_5. The patent also recites a large number of optional ingredients in varying amounts including 0-3% Al_2O_3 and 0-25% ZnO. Ta_2O_5 comprises no part of the present inventive glasses and, even ignoring the presence of Ta_2O_5, none of the working examples provided in the patent had a composition within the ranges required in the present inventive glasses.

U. S. Patent No. 4,544,974 recites glass compositions suitable for bonding metals or metal oxides into a composite structure. The glasses consist essentially, in mole percent, of 10-40% alkali metal or alkaline earth metal oxide, 0-25% CuO or ZnO, 5-15% Al_2O_3, 0-25% B_2O_3, 0-30% SiO_2, and 10-35% P_2O_5, wherein at least one of B_2O_3, CuO, SiO_2, and ZnO is present. B_2O_3 and SiO_2 are not required constituents in the present inventive glasses; the Al_2O_3 content of the glasses disclosed in the patent is higher than desired in the present inventive glasses; and, even ignoring the high Al_2O_3 levels, the working examples provided in the patent had compositions outside the ranges demanded in the present inventive glasses.

"Oxide Glasses of Very Low Softening Point. Parts 1 and 2. Preparation and Properties of Some Lead Phosphate Glasses," N. H. Ray et al., Glass Technology 14, No. 2, pages 50-59, April 1973, provides an extensive study of a wide variety of phosphate-based glasses, including R_2O-ZnO-P_2O_5 glasses. However, none of the glasses had a composition coming within the ranges of the present invention.

Description of Preferred Embodiments

Table I records a number of glass compositions, expressed in terms of mole percent on the oxide basis, operable in the present invention. Table IA reports the same compositions, but wherein the values of the individual components have been converted to weight percent. The actual batch ingredients for the glasses can comprise any materials, either the oxides or other compounds, which,

upon being melted together, will be converted into the desired oxides in the proper proportions. For example, Li_2CO_3 is conveniently employed as the source of Li_2O. Because it is not known with which cation it is combined and because the amount included was relatively quite small, the fluoride content is simply recorded in percent in addition to the base glass composition.

The batch materials were compounded, ballmilled together to aid in securing a homogeneous melt, and then charged into silica crucibles. After placing lids thereon, the crucibles were introduced into a furnace operating at about 1000°C and maintained at that temperature for about 3 hours. Each melt was poured into a steel mold to produce a rectangular glass slab having dimensions of about 8"x4"x0.5" and the glass slab annealed overnight at 300°C.

Rectangular tab-shaped pieces weighing about 30-40 grams were cut from the slabs and heat treated in cups of aluminum foil to temperatures within the range of 350°-450°C, and glass cane was hand drawn from each cup to obtain a close approximation of the working temperature of the glass.

Whereas the above description reflects laboratory melting and forming practice only, it will be appreciated that the recited compositions are capable of being melted in large scale melting units and shaped into desired configurations utilizing forming techniques conventional in the glassmaking art.

Table I (Mole %)

	1	2	3	4	5	6	7
P_2O_5	35.4	32.0	35.0	32.0	32.0	34.0	35.0
Al_2O_3	3.1	2.0	2.0	1.0	2.0	3.3	2.0
Li_2O	7.8	9.0	10.0	10.0	10.0	9.9	10.0
Na_2O	7.8	9.0	10.0	10.0	10.0	9.9	10.0
ZnO	45.9	48.0	43.0	47.0	46.0	43.0	38.0
CaO	-	-	-	-	-	-	3.0
MgO	-	-	-	-	-	-	2.0
F_2	-	-	-	-	-	2.0	-

	8	9	10	11	12	13
P_2O_5	35.0	35.0	33.0	33.0	33.0	31.0
Al_2O_3	2.0	2.0	2.0	2.0	3.0	2.0
Li_2O	7.0	22.0	10.0	10.0	5.0	-
Na_2O	7.0	-	10.0	-	7.0	10.0
ZnO	39.0	33.0	45.0	45.0	45.0	47.0
Cu_2O	10.0	-	-	-	-	-
CaO	-	8.0	-	-	-	-
K_2O	-	-	-	10.0	7.0	10.0

	14	15	16	17	18	19
P_2O_5	33.0	33.0	32.0	33.0	33.0	33.0
Al_2O_3	2.0	2.0	-	-	2.0	2.0
Li_2O	8.0	8.0	9.0	10.0	6.0	8.0
Na_2O	12.0	12.0	9.0	10.0	7.0	12.0
ZnO	25.0	30.0	50.0	43.0	45.0	15.0
K_2O	-	-	-	-	7.0	-
PbO	20.0	-	-	-	30.0	-
SnO	-	15.0	-	-	-	-
B_2O_3	-	-	-	4.0	-	-

Table I (Mole %) (continued)

	20	21	22	23	24	25	26
P_2O_5	33.0	33.0	33.0	33.0	33.0	33.0	33.0
Al_2O_3	2.0	2.0	2.0	2.0	2.0	2.0	-
Li_2O	8.0	-	10.0	-	6.0	4.0	6.0
Na_2O	12.0	17.0	10.0	8.0	6.0	10.0	8.0
ZnO	25.0	40.0	35.0	40.0	46.0	41.0	45.0
K_2O	-	8.0	10.0	17.0	7.0	10.0	8.0
SnO	20.0	-	-	-	-	-	-

	27	28	29	30	31	32
P_2O_5	33.0	31.6	33.0	37.0	38.0	41.0
Al_2O_3	2.0	1.9	2.0	2.0	2.0	2.0
Li_2O	6.0	9.8	6.0	9.0	22.0	9.0
Na_2O	7.0	9.6	7.0	9.0	-	9.0
ZnO	41.0	33.5	41.0	43.8	38.0	39.0
MnO	4.0	-	-	-	-	-
SnO	-	9.7	4.0	-	-	-
ZrO_2	-	3.9	-	-	-	-
K_2O	7.0	-	7.0	-	-	-

Table IA (Weight %)

	1	2	3	4	5	6	7
P_2O_5	51.3	47.9	51.8	48.4	48.3	50.6	52.7
Al_2O_3	3.3	2.1	2.1	1.1	2.1	3.5	2.1
Li_2O	2.4	2.8	3.1	3.2	3.2	3.1	3.2
Na_2O	4.9	5.9	6.5	6.6	6.6	6.3	6.6
ZnO	38.1	41.2	36.5	40.7	39.8	36.5	32.8
CaO	-	-	-	-	-	-	1.8
MgO	-	-	-	-	-	-	0.8
F_2	-	-	-	-	-	1.7	-

Table IA (Weight %) (continued)

	8	9	10	11	12	13
P_2O_5	47.7	55.5	49.5	47.9	47.3	44.1
Al_2O_3	1.9	2.2	2.2	2.1	3.1	2.0
Li_2O	2.0	7.4	3.2	3.1	1.5	-
Na_2O	4.9	-	6.5	-	4.4	6.2
ZnO	30.5	29.9	38.6	37.4	37.0	38.3
Cu_2O	13.7	-	-	-	-	-
CaO	-	5.0	-	-	-	-
K_2O	-	-	-	9.6	6.6	9.4

	14	15	16	17	18	19
P_2O_5	37.9	45.4	48.1	49.9	47.3	34.0
Al_2O_3	1.6	1.9	-	-	2.1	1.5
Li_2O	1.9	2.3	2.9	3.2	2.4	1.7
Na_2O	6.0	7.2	5.9	6.6	4.4	5.4
ZnO	16.4	23.6	43.1	37.3	37.1	8.8
K_2O	-	-	-	-	6.7	-
PbO	36.1	-	-	-	-	48.5
SnO	-	19.5	-	-	-	-
B_2O_3	-	-	-	3.0	-	-

	20	21	22	23	24	25	26
P_2O_5	44.3	47.2	48.9	45.8	47.8	47.3	48.0
Al_2O_3	1.9	2.0	2.1	2.0	2.0	2.0	-
Li_2O	2.3	-	3.1	-	1.8	1.2	1.8
Na_2O	7.0	10.6	6.5	4.9	4.4	6.3	5.1
ZnO	19.2	32.7	29.7	31.7	37.3	33.7	37.4
K_2O	-	7.5	9.8	15.6	6.7	9.5	7.7
SnO	25.4	-	-	-	-	-	-

Table IA (Weight %) (continued)

	27	28	29	30	31	32
P_2O_5	48.0	44.5	46.7	53.7	49.5	53.9
Al_2O_3	2.0	1.9	2.0	2.0	2.2	2.2
Li_2O	1.8	2.9	1.8	2.8	9.3	3.9
Na_2O	4.4	5.9	4.2	5.7	6.0	5.8
ZnO	34.1	27.1	33.3	35.8	33.0	34.2
MnO	2.9	-	-	-	-	-
SnO	-	12.9	5.4	-	-	-
ZrO_2	-	4.8	-	-	-	-
K_2O	6.7	-	6.5	-	-	-

Samples having the approximate dimensions of 35 x 25 x 15 mm were cut from each glass slab and then ground and polished for testing the chemical durability thereof. In one test each sample was carefully weighed and then immersed into a bath of boiling water. After a residence time of six hours, the sample was removed from the bath, dried in the ambient environment, and thereafter weighed to determine any loss of weight by the sample. In a second test each sample was carefully weighed and then immersed into a bath operating at 75°C of a 0.3% by weight aqueous solution of SUPER SOILAX detergent marketed by Economics Laboratories, St. Paul, Minnesota, the solution exhibiting a pH of about 10. After a dwell period of 24 hours, the sample was removed from the bath, dried in the ambient environment, and reweighed to measure any weight loss. In a third test each sample was carefully weighed and then introduced into an autoclave. The temperature within the autoclave was raised to 125°C and a steam atmosphere of 33 psi generated. After an exposure of four hours, the sample was removed from the autoclave, dried in the ambient environment, and again weighed to determine any loss in weight. The Tg of the glass was measured utilizing standard differential scanning calorimetry techniques.

Table II reports the percent weight loss in the boiling water test (H_2O), the percent weight loss in the SUPER SOILAX test (SUPER), the percent weight loss in the steam test (Steam), the Tg of the glass in °C, and the working temperature of the glass in °C as determined by pulling cane (Pull). In certain instances, the samples exhibited a frosted appearance after exposure to the steam test. That phenomenon is noted by the designation (Fr). One example crystallized (Cryst) during the pull test.

Table II

	1	2	3	4	5	6	7
H_2O	-	0.00	0.02	0.02	0.00	0.00	0.00
SUPER	0.00	0.05	0.83	-	-	0.09	1.8
Tg	370	355	-	-	-	350	354
Pull	-	450	425	425	425	425	425

	8	9	10	11	12	13
H_2O	0.00	0.02	0.00	0.02	0.00	0.00
SUPER	0.03	1.35	0.05	0.06	-	0.09
Steam	-	-	-	0.00Fr	0.00Fr	0.05
Tg	333	369	343	358	-	366
Pull	430	450	430	450	450	450

	14	15	16	17	18	19
H_2O	-	-	0.05	0.00	0.00	0.00
SUPER	0.05	0.08	-	-	-	-
Steam	-	-	-	-	0.03	0.09Fr
Tg	323	-	-	-	335	-
Pull	-	410	425	425	430	Cryst

Table II (continued)

	20	21	22	23	24	25	26
H_2O	0.00	0.03	0.00	0.00	0.00	0.00	0.00
SUPER	-	2.0	3.1	-	0.11	-	-
Steam	0.02Fr	0.00	0.15Fr	0.32Fr	0.00	0.03	0.41
Pull	375	430	415	430	430	415	400

	27	28	29	30	31	32
H_2O	0.00	0.00	0.00	0.52	0.75	1.21
SUPER	-	-	0.31	-	-	-
Steam	0.00	-	0.00	-	-	-
Tg	-	313	330	-	-	-
Pull	435	-	425	420	425	415

The measures of resistance to attack by water exhibited by Examples 1-29 are very exceptional for phosphate-based glass compositions, and are particularly noteworthy since the glasses demonstrate such low transition and working temperatures. The sharp deterioration in chemical durability occurring in glass compositions even slightly outside the ranges prescribed in the inventive glasses is immediately evident with a review of Examples 30-32. Hence, in Example 30 additions of Al_2O_3 and/or substitutions of Cu_2O for R_2O and/or ZnO would be required to improve their durability to the level of that exhibited by Example 3 which is lower in P_2O_5 content and within the most preferred region of compositions. Example 31 clearly illustrates the need for at least two alkali metal oxides in the glass. In Example 32 the level of P_2O_5 is too high. The high resistance to moisture attack renders the inventive glasses eminently suitable for a wide range of applications including, for example, food service, electronic devices, optical and ophthalmic lenses, and coatings for optical waveguides. Furthermore, because the viscosity relationships exhibited by the inventive glasses at relatively low working temperatures render them capable of being shaped

into articles of complex configurations through extrusion, injection molding, and other techniques conventionally employed in the plastic forming art, the range of products for which the inventive glass-ceramics are useful is greatly broadened.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A glass exhibiting a transition temperature below 450°C, a working temperature below 500°C, and excellent resistance to attack by water and mild aqueous alkaline solutions, said glass comprising, expressed in terms of mole percent on the oxide basis, at least 65% total of 12-55% ZnO, 28-40% P_2O_5, and 10-35% R_2O, wherein R_2O consists of at least two alkali metal oxides in the indicated proportions selected from the group consisting of 0-25% Li_2O, 0-25% Na_2O, and 0-25% K_2O, and up to 35% total of optional ingredients in the indicated proportions selected from the group consisting of 0-6% Al_2O_3, 0-8% B_2O_3, 0-8% $Al_2O_3+B_2O_3$, 0-15% Cu_2O, 0-5% F, 0-35% PbO, 0-35% SnO, 0-35% PbO+SnO, 0-5% ZrO_2, 0-4% SiO_2, and 0-15% MgO+CaO+SrO+BaO+MnO, consisting of 0-10% MgO, 0-10% CaO, 0-10% SrO, 0-12% BaO, and 0-10% MnO.

2. A glass according to claim 1 containing 0.75-6% Al_2O_3 and/or 1-8% B_2O_3, the total $Al_2O_3+B_2O_3$ not exceeding 8%.

3. A glass according to claim 1 containing 30-55% ZnO, 30-38% P_2O_5, 0-4% Al_2O_3, 0-10% PbO, 0-10% SnO, and 10-30% R_2O, wherein R_2O consists of 3-12% Li_2O, 4-18% Na_2O, and 0-12% K_2O.

4. A glass according to claim 1 containing 0-5% CaO.

5. A glass according to claim 4 containing 6-15% CaO+BaO.

6. A glass according to claim 1 wherein the sum of $R_2O+Al_2O_3$ and/or $B_2O_3+ZnO+P_2O_5+PbO+SnO$ totals at least 85%.

7. A glass according to claim 1 containing 23-55% ZnO.

8. A glass according to claim 3 wherein the sum of $R_2O+Al_2O_3+ZnO+P_2O_5+PbO+SnO$ totals at least 85%.

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9. A glass according to claim 3 consisting essentially of 12-25% R_2O, wherein R_2O consists of at least two alkali metal oxides in the indicated proportions of 3-12% Li_2O, 4-13% Na_2O, and 0-12% K_2O, 30-49% ZnO, 1-3.5% Al_2O_3, 30-36% P_2O_5, and 0-10% SnO, the sum of $R_2O+Al_2O_3+ZnO-P_2O_5+SnO$ totals at least 85%.

10. A glass according to any one of the previous claims substantially as herein described with reference to any one of the Examples.

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