27
4-13-81
J. A. Wilder, Jr.
SAND80-2192
UNLIMITED RELEASE

UC-25

GLASS CERAMICS FOR SEALING TO HIGH-THERMAL-
EXPANSION ALLOYS

MASTER

JAMES A. WILDER, JR.

Prepared by Sandia Laboratories, Albuquerque, New Mexico 87185
and Livermore, California 94550 for the United States Department of
Energy under Contract DE-AC04-76DP00789.

Printed March 1981

Sandia National Laboratories

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Issued by Sandia National Laboratories, operated for the
United States Department of Energy by Sandia Corporation

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Printed in the United States of America

Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

Price: Printed Copy \$4.50; Microfiche \$3.00

PAGES 1 to 2
WERE INTENTIONALLY
LEFT BLANK

SAND80-2192

This Unlimited Release
Printed October 1980GLASS CERAMICS FOR SEALING TO
HIGH-THERMAL-EXPANSION METALS

by

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

J. A. Wilder, Jr. (5845)
Sandia National Laboratories
Albuquerque, NM 87185

ABSTRACT

We studied glass ceramics, formulated in the $\text{Na}_2\text{O} \cdot \text{CaO} \cdot \text{P}_2\text{O}_5$, $\text{Na}_2\text{O} \cdot \text{BaO} \cdot \text{P}_2\text{O}_5$, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$, and $\text{Li}_2\text{O} \cdot \text{BaO} \cdot \text{P}_2\text{O}_5$ systems to establish their suitability for sealing to high thermal expansion metals, e.g. aluminum, copper, and 300 series stainless steels. Glass ceramics in $\text{Na}_2\text{O} \cdot \text{CaO} \cdot \text{P}_2\text{O}_5$ and $\text{Na}_2\text{O} \cdot \text{BaO} \cdot \text{P}_2\text{O}_5$ systems have coefficients of thermal expansion in the range $140 \times 10^{-7} \cdot ^\circ\text{C}^{-1} \leq \alpha \leq 225 \times 10^{-7} \cdot ^\circ\text{C}^{-1}$ and fracture toughness values generally greater than those of phosphate glasses; they are suitable for fabricating seals to high thermal expansion metals. Crystal phases include NaPO_3 , $(\text{NaPO}_3)_3$, $\text{NaBa}(\text{PO}_3)_3$, and $\text{NaCa}(\text{PO}_3)_3$. Glass ceramics formed in the $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$ systems have coefficients of thermal expansion greater than $240 \times 10^{-7} \cdot ^\circ\text{C}^{-1}$, but they have extensive microcracking. Due to their low thermal expansion values ($\alpha \leq 120 \times 10^{-7} \cdot ^\circ\text{C}^{-1}$), glass ceramics in the $\text{Li}_2\text{O} \cdot \text{BaO} \cdot \text{P}_2\text{O}_5$ system are unsuitable for sealing to high thermal expansion metals.

deq
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *eb*

CONTENTS

	Page
I. INTRODUCTION.	6
II. BACKGROUND.	7
III. EXPERIMENTAL PROCEDURE.	10
A. Materials	10
B. Glass Ceramic Formation	11
C. Thermal Expansion Coefficient	11
D. Crystal Phase Identification.	11
E. Fracture Toughness Measurements	11
F. Chemical Durability Measurements.	12
IV. RESULTS	12
A. $\text{Na}_2\text{O} \cdot \text{CaO} \cdot \text{P}_2\text{O}_5$ and $\text{Na}_2\text{O} \cdot \text{BaO} \cdot \text{P}_2\text{O}_5$ Systems	12
B. $\text{Li}_2\text{O} \cdot \text{BaO} \cdot \text{P}_2\text{O}_5$ and $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$ Systems	15
C. Chemical Durability Results	16
V. APPLICATIONS.	18
VI. SUMMARY	19
VII. ACKNOWLEDGEMENTS.	20
VIII. REFERENCES.	21

FIGURES

Figure		Page
1.	Change in length versus temperature for cristobalite SiO_2 and the cristobalite form of AlPO_4 (Fig. 5 of Ref. 5).	25
2.	Schematic illustration of temperature versus time cycle for controlled crystallization of glasses.	26
3.	Thermal expansion coefficients of glass ceramic materials versus thermal expansion coefficients of parent glasses.	27
4.	Thermal expansion coefficients of glass ceramic materials in the $\text{Na}_2\text{O}\cdot\text{BaO}\cdot\text{P}_2\text{O}_5$ system versus thermal expansion coefficient ranges for aluminum, copper, and steel alloys.	28

TABLES

Table		Page
1	Variation in Thermal Expansion Coefficients of Glass Ceramics as a Function of Parent Glass Composition and Heat Treatment Schedules.	22
2	Variation in Fracture Toughness of Glass Ceramics as a Function of Heat Treatment Schedules.	23
3	Leach Rate Data for Glass Ceramic Materials in Deionized Water.	24

I. INTRODUCTION

"High" thermal expansion metals, e.g. copper, 300 series stainless steels, and aluminum alloys are attractive for fabricating hermetic seals. Commercial use of these metals has been restricted to compression seals for 300 series stainless steels and copper; aluminum seals are not available. Aluminum alloys, due to their light weight, low cost, ease of machineability, and low hydrogen permeability are attractive casing materials for use in vacuum tubes, hermetic packages, cable connectors, and detonator components. Previous attempts by commercial suppliers to formulate glasses or glass ceramics which can be hermetically sealed to aluminum alloys have been unsuccessful due to the high coefficient of thermal expansion ($\alpha \approx 230 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$) and low melting temperature ($\sim 650^\circ\text{C}$) of aluminum alloys.

Our previous work described several glasses, based on phosphorous pentoxide (P_2O_5), which we developed and hermetically sealed to copper, stainless steel, and aluminum.¹ Desirable properties of these glasses include high coefficients of thermal expansion, low sealing temperatures, low helium permeability, and high chemical durability over selected composition ranges. They are mechanically weaker and more susceptible to thermal shock than silicate glasses, however.

Improved mechanical strength and thermal shock characteristics, as well as increased flexibility in tailoring other properties by formation of crystal phases in a glass, provided the principal motivation for development of phosphate glass ceramics. However, fabrication of a glass ceramic-to-aluminum seal imposes the additional

constraint that crystallization temperatures, in addition to the sealing temperature, must be below the melting point of aluminum alloys.

This report discusses glass ceramic materials that we have developed to seal to these metals, particularly to aluminum.

II. BACKGROUND

Glass ceramic formation, defined as controlled growth of crystal phases in a glass, has received little attention in glass systems based on phosphorous pentoxide (P_2O_5). This situation has been fostered by the hygroscopic nature of many phosphate glasses and the resultant lack of widespread commercial utilization. This section summarizes relevant previous work on P_2O_5 based glass ceramics and crystal phases.

Gutzow et al.² and Rindone and Ryder³ examined crystallization in a $NaPO_3$ glass. Gutzow et al.² reported that orthorhombic $Na_3(P_3O_9)$ with a cyclic structure is formed by reconstructive crystallization. In addition, they examined the effect of different noble metals as nucleating agents and found their effectiveness decreased in the order $Au < Ag < Rh < Pd < Pt < Ir$. Rindone and Ryder³ examined the effects of concentration of Pt and Na_2O in this glass and found small amounts of Pt cause phase separation while higher concentrations induce crystallization. In addition, for a given Pt concentration, increasing Na_2O concentration leads to crystallization.

Several workers, including Beck,⁴ Hummel,⁵ and Moriya, Akao, and Natano,⁶ studied crystallization in aluminophosphate systems. Beck⁴ and Hummel⁵ found aluminum orthophosphate ($AlPO_4$) crystal

structures isostructural with crystalline silicon dioxide (SiO_2). Crystalline SiO_2 can exist in the polymorphic forms; quartz, cristobalite, or tridymite. Each crystal structure consists of SiO_4 tetrahedra which are arranged differently for a particular crystal type. Transformation between crystal types involves the breaking and rearrangement of molecular bonds. These SiO_2 crystal forms contain a low temperature form and a high temperature form which arises from displacement of the SiO_4 tetrahedra without bond rupture. Temperature inversions occur at:

α Quartz $\rightarrow$ β Quartz: $\sim 570^\circ\text{C}$

α Tridymite $\rightarrow$ β Tridymite: $\sim 120^\circ\text{C}$ to 160°C

α Cristobalite $\rightarrow$ β Cristobalite: $\sim 200^\circ\text{C}$ to 275°C .

Beck⁴ and Hummel⁵ show that AlPO_4 crystals existed in three polymorphic forms and exhibited high and low temperature inversions analogous to crystalline silicon dioxide. These forms are identified as berlinite (analogous to quartz), tridymite form, and cristobalite form. Temperature inversions occur at:

α Berlinite $\rightarrow$ β Berlinite: $\sim 586^\circ\text{C}$

α Tridymite Form $\rightarrow$ β Tridymite Form: $\sim 90^\circ\text{C}$ to 96°C

α Cristobalite Form $\rightarrow$ β Cristobalite Form: $\sim 210^\circ\text{C}$.

Since volume changes accompany the temperature inversions, a discontinuity is produced in the thermal expansion coefficient. Figure 1 shows the change in length versus temperature for SiO_2 cristobalite and the cristobalite form of AlPO_4 .

Studies of glass ceramic formation in ternary $\text{Al}_2\text{O}_3 \cdot \text{B}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$ systems have been performed by MacDowell and Wilson⁷ and Klein, Kolbeck, and Quackenbush.⁸ MacDowell and Wilson⁷ examined compositions which consisted of a minimum of 75% (Al_2O_3 , B_2O_3 , P_2O_5) plus 25% other oxide components. Their glass ceramics had thermal expansion coefficients in the range of 90×10^{-7} to $180 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$. However, crystallization temperatures were usually greater than 650°C (melting point of aluminum $\approx 660^\circ\text{C}$).

Klein, et al.⁸ found that glass ceramics readily formed without use of nucleating agents, and thermal expansion coefficients of the glass ceramics were in the range of 90×10^{-7} to $140 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$. However, as in MacDowell and Wilson's⁷ study, crystallization temperatures were frequently above aluminum's melting point.

In their studies of $\text{Al}_2\text{O}_3 \cdot \text{B}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$ systems, the authors did not correlate the crystal phases present with the thermal expansion coefficient of a particular glass ceramic.^{7,8} However, the high expansion coefficients they observed were probably due to the presence of AlPO_4 crystals. The presence of large fractions of crystalline quartz, cristobalite, or tridymite in silicate glass ceramics utilized in ceramic/metal sealing applications is undesirable because stresses are generated at the seal interface due to discontinuous changes in thermal expansion. Similarly, presence of AlPO_4 in phosphate glass ceramics creates stresses at the interface.

Brown and Hummel⁹ formulated a series of polycrystalline ceramics in the zinc phosphate and magnesium phosphate systems and characterized the thermal expansion coefficients. They found these ceramics to possess relatively low expansion coefficients with

values of:

α - $\text{Zn}(\text{PO}_3)_2$ [alpha zinc metaphosphate], $\alpha = 17 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$

β - $\text{Zn}(\text{PO}_3)_2$ [beta zinc metaphosphate], $\alpha = 61 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$

and $\text{Mg}(\text{PO}_3)_2$ [magnesium metaphosphate], $\alpha = 90 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$

being obtained.

In summary, previous studies of phosphate glass ceramics have not identified systems which are suitable for sealing to aluminum alloys. These systems either have sealing and/or crystallization temperatures above the melting point of aluminum or thermal expansion coefficients which do not match the metal's expansion coefficient.

III. EXPERIMENTAL PROCEDURE

A. Materials

We prepared glasses in 100 to 200 gram batches by mixing metal oxide or metal carbonate powders with ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$). After mixing, the powders were transferred to a platinum crucible in a well-vented melt furnace. The powders were calcined at 300°C to slowly eliminate H_2O and NH_3 vapors. After calcining, the temperature was increased until a fluid melt occurred. The melting temperature, a function of glass composition, was below 1000°C for high alkali oxide concentration and above 1000°C for high alkaline-earth oxide concentrations. Melts were generally held at the upper temperature for one hour, cast onto an $\sim 200^\circ\text{C}$ hot plate and transferred to an annealing furnace. We estimated initial coarse annealing temperatures from differential thermal analysis results from the

as-cast samples and developed final annealing schedules to yield stress-free samples based on polariscopic examination of the glass.

B. Glass Ceramic Formation

After annealing, we transferred glass samples to a heat treatment oven to induce crystallization, by heating to the nucleation temperature at 5 to 10 $\frac{^{\circ}\text{C}}{\text{min}}$ and holding for a predetermined time followed by continued heating to a growth temperature and holding. Finally, the crystallized sample was cooled to room temperature at 0.5 to 1 $\frac{^{\circ}\text{C}}{\text{min}}$. Figure 2 schematically illustrates the crystallization cycle.

C. Thermal Expansion Coefficient

The linear thermal expansion, defined as $\alpha = \frac{1}{L} \frac{\Delta L}{\Delta T}$ where L = sample length and ΔL and ΔT are changes in sample length and temperature, respectively, was measured on a fused silica pushrod dilatometer. Sample geometry was a bar of approximately 3 x 6 mm cross section and 25.4 mm length.

D. Crystal Phase Identification

Crystal phases were tentatively identified by two methods. Endothermic melting temperatures, determined from Differential Thermal Analysis, in the glass ceramic were compared with known crystal phase melting points. D-spacings determined from X-ray powder diffraction patterns were compared with reference values.

E. Fracture Toughness Measurements

Fracture toughness values were obtained using a Terra Tek Fractometer, Model 3401.¹⁴ This apparatus uses a sample of 19.05 mm

height and 12.70 mm diameter which has a V-shaped slot cut in one end. The sample is positioned with an inflatable bladder situated in the slot. A fluid inflates the bladder causing the slot to open. Pressure in the bladder is recorded and used to calculate K . .

F. Chemical Durability Measurements

Leach rates in 100 ml of deionized water ($6.1 \leq \text{initial pH} \leq 6.3$) were measured on cylindrically shaped samples suspended from either platinum wire or nylon thread. Leaching solutions were maintained at 20°C or 70°C.

IV. RESULTS

A. $\text{Na}_2\text{O} \cdot \text{CaO} \cdot \text{P}_2\text{O}_5$ and $\text{Na}_2\text{O} \cdot \text{BaO} \cdot \text{P}_2\text{O}_5$ Systems

Glass ceramics have been formed in both the $\text{Na}_2\text{O} \cdot \text{CaO} \cdot \text{P}_2\text{O}_5$ and $\text{Na}_2\text{O} \cdot \text{BaO} \cdot \text{P}_2\text{O}_5$ glass systems. Thermal expansion coefficients of the glass ceramics which match copper ($165 \times 10^{-7} \text{ } ^\circ\text{C}^{-1} \leq \alpha \leq 210 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$), 300 series steel ($\alpha \sim 190 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$) or aluminum alloys ($200 \times 10^{-7} \text{ } ^\circ\text{C}^{-1} \leq \alpha \leq 240 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$) have been obtained. Table I lists a series of sodium barium phosphate and sodium calcium phosphate glasses which were crystallized along with the crystallization cycle and thermal expansion coefficients after heat treatment. Table I reveals that expansion coefficients can be varied by adjusting the parent glass composition and/or the temperatures and times of the crystallization cycle. For glasses in the $\text{Na}_2\text{O} \cdot \text{BaO} \cdot \text{P}_2\text{O}_5$ system crystallized on a cycle of 2 hr. @ 400°C plus 2 hr. @ 450°C, the thermal expansion decreases from $230 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$ to $170 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$ as barium oxide replaces sodium oxide in the parent glass composition. A similar effect was observed in the $\text{Na}_2\text{O} \cdot \text{CaO} \cdot \text{P}_2\text{O}_5$ system. In each case, heat treatment temperatures

induced crystallization below the melting point of aluminum ($T_{mp} \sim 650^\circ\text{C}$).

In Figure 3, thermal expansion coefficients of glass ceramic materials are compared with the parent glasses' expansion for a $\text{Na}_2\text{O} \cdot \text{BaO} \cdot \text{P}_2\text{O}_5$ series. Glass ceramic samples were formed by heat treating for 2 hr. @ 400°C plus 2 hr. @ 450°C . Glass ceramics with higher expansion values than the parent glass were produced from glasses with higher sodium oxide concentration. Glasses with higher barium oxide concentrations frequently produce glass ceramics with lower expansion coefficients.

Often we observed that the coefficient of thermal expansion of a glass, below its transformation range, is similar to that of a crystal of similar composition. This effect arises because the coefficient of thermal expansion is primarily dependent on the local arrangement of nearest-neighbor atoms which are similar in the glassy and crystalline form of the same substance.¹¹ X-ray diffraction analysis has tentatively identified several crystallographic forms of sodium metaphosphate in the glass ceramics with higher thermal expansion coefficients. A sodium metaphosphate glass fabricated in our laboratory has an expansion coefficient of $240 \times 10^{-7}^\circ\text{C}^{-1}$ over the temperature range 25°C to 250°C . Since it is probable that the glass and crystal's expansion coefficients are similar in magnitude, we believe the presence of sodium metaphosphate crystal phases accounts for expansion coefficients, $> 200 \times 10^{-7}^\circ\text{C}^{-1}$, in certain of these glass ceramics.

Figure 4 demonstrates the capability of formulating glass ceramics which have expansion coefficients matched to high expansion alloys of aluminum, steel, or copper. Thermal expansion coefficients

of glass ceramics are plotted versus the molar ratio $\left(\frac{\text{BaO}}{\text{Na}_2\text{O} + \text{BaO}} \right)$ of the parent glass composition in a $(50-X)\text{Na}_2\text{O} \cdot X\text{BaO} \cdot 50\text{P}_2\text{O}_5$ (mole%) system. Each glass was crystallized on a 2 hr. @ 400°C plus 2 hr. @ 450°C cycle. Also shown are the expansion coefficient ranges for aluminum, 300 series steel, and copper alloys.

Crystal phase identification has been limited by lack of crystallographic data for many phosphate crystals. Tentative identification of phases indicates that NaPO_3 (sodium metaphosphate) and/or $(\text{NaPO}_3)_3$ (sodium trimetaphosphate) crystal phases are present in the glass ceramics with expansion coefficients equal to aluminum alloys ($\alpha \approx 230 \times 10^{-7} \text{ }^\circ\text{C}^{-1}$). Glass ceramics with lower expansion coefficients ($\alpha < 200 \times 10^{-7} \text{ }^\circ\text{C}^{-1}$) have crystal phases tentatively identified as $\text{NaBa}(\text{PO}_3)_3$ (sodium barium phosphate), $\text{Ba}_3(\text{PO}_4)_2$ (barium phosphate), $\text{NaCa}(\text{PO}_3)_3$ (sodium calcium phosphate), and $\text{Na}_4\text{Ba}(\text{PO}_3)_6$ (sodium barium phosphate).

The emphasis to investigate glass ceramics stems from the increased flexibility in tailoring properties for a particular application. In particular, glass ceramic materials often show improvement in mechanical strength compared to the glasses from which they were formed.¹³

Preliminary results indicate a definite improvement in the mechanical properties of the phosphate glass ceramics compared to the glasses. In the $(50-X)\text{Na}_2\text{O} \cdot X\text{BaO} \cdot 50\text{P}_2\text{O}_5$ (mole%) glass system, fracture toughness values increased from 0.43 to 0.53 $\text{MPa(m)}^{1/2}$ for increasing x ($10 \leq x \leq 40$). In the sodium barium alumina phosphate glass ceramics, fracture toughness values in the range 0.45 to 0.65 $\text{MPa(m)}^{1/2}$ have been obtained. Table 2 summarizes the results. Compositions are

given in terms of glass composition prior to crystallization. Selection of appropriate heat treatment schedule can increase fracture toughness values by 35% without altering the thermal expansion coefficient.

B. $\text{Li}_2\text{O} \cdot \text{BaO} \cdot \text{P}_2\text{O}_5$ and $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$ Systems

The $\text{Li}_2\text{O} \cdot \text{BaO} \cdot \text{P}_2\text{O}_5$ and $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$ systems exhibit desirable properties in the glassy state. These include high coefficients of thermal expansion ($150 \times 10^{-7} \text{ } ^\circ\text{C}^{-1} \leq \alpha \leq 240 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$), low sealing temperatures ($< 400^\circ\text{C}$), low helium permeabilities ($< 10^{-9} \frac{\text{molecules}}{\text{cm-sec-atm}}$) and good resistance to aqueous corrosion over certain composition ranges.^{1,10} However, in the cerammed state, these materials possess undersirable characteristics. Results are summarized for completeness.

Glass ceramics formed in the $\text{Li}_2\text{O} \cdot \text{BaO} \cdot \text{P}_2\text{O}_5$ system form crystal phases which lower the thermal expansion coefficient from $\sim 160 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$ in the glassy state to values less than $110 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$ in the cerammed state. The large difference in thermal expansion between aluminum and the glass ceramics would generate significantly high stresses at the aluminum/glass ceramic interface and cause seal failure. In addition, crystallization preferentially occurs on the surface of the glass, resulting in extensive void formation in the body of the ceramic article. These drawbacks presently make this system unacceptable for sealing to high thermal expansion metals.

Glass ceramics have been formed in the $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$ system with thermal expansion coefficient values of $250 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$. However, these ceramic materials exhibit extensive microcracking and are mechanically weak.

C: Chemical Durability Results

A limited leach rate study was performed on six phosphate-based glass ceramics. Parent glass compositions, crystallization cycles, leach rates, and comments on the structural integrity are given in Table 3.

The glass ceramics, based on leach rate measurements, show moderate to good resistance to aqueous corrosion, but their resistance is lower than that of our most durable phosphate glasses, i.e. phosphate glass ceramic leach rate $\approx 5 \times 10^{-7} \frac{\text{gm}}{\text{cm}^2 \cdot \text{min}}$ versus a phosphate glass leach rate of $\approx 2 \times 10^{-9} \frac{\text{gm}}{\text{cm}^2 \cdot \text{min}}$ at 20°C. (The leach rate of soda-lime window glass is $\approx 5 \times 10^{-8} \frac{\text{gm}}{\text{cm}^2 \cdot \text{min}}$ at 20°C.)

For glass ceramic materials containing 40 mole% of Na₂O in the parent glass composition, an increase in Al₂O₃ concentration increases the resistance to aqueous corrosion (i.e. lower leach rates) at room temperature. We observed that attack occurs in the residual glass phase surrounding the crystal grains. We believe that Al₂O₃ is remaining in the residual glass phase and increasing its corrosion resistance. This interpretation is supported by the absence of aluminum phosphate crystal phases in X-ray powder diffraction patterns. Analogous behavior has been observed in phosphate glasses where the leach rate decreased from $2 \times 10^{-4} \frac{\text{gm}}{\text{cm}^2 \cdot \text{min}}$ to $3 \times 10^{-8} \frac{\text{gm}}{\text{cm}^2 \cdot \text{min}}$ in a series of glasses of composition 40Na₂O·10BaO·XAl₂O₃·(50-X)P₂O₅ (mole%) as X increased from 0 to 5.

In the second group of glass ceramics containing 30, 27, and 29 mole% of Na₂O respectively, a large variation in the room temperature leach rates was observed. Again, corrosion occurred in the residual glass phase surrounding the crystal grains. Tentative identification

of the crystal phase using DTA analysis and X-ray powder diffraction analysis shows identical crystal phases in each of the glass ceramics. However, microstructure studies indicate large differences in the volume fraction of the crystal phases which results in differences in the composition of the residual glass phase. We believe the compositional variation of the residual glass phase accounts for the variations in the leach rates.¹³

The interpretation of large variations in leach rates caused by compositional variations is supported by our results for phosphate glasses. For example, in the composition series $(50-X)\text{Na}_2\text{O} \cdot X\text{BaO} \cdot 50\text{P}_2\text{O}_5$ (mole%) the leach rate decreased from $1.5 \times 10^{-4} \frac{\text{gm}}{\text{cm}^2 \cdot \text{min}}$ to $2 \times 10^{-9} \frac{\text{gm}}{\text{cm}^2 \cdot \text{min}}$ as X increased from 10 to 35. In order to compute the exact composition of the residual glass phase, we must conclusively identify the crystal phases and their volume fraction. If the above interpretation is correct, the leach rate of a glass, which has the composition of the residual glass phase, should equal the leach rate of the glass ceramic.

We have developed a phosphate glass ceramic of good corrosion resistance (leach rate $\approx 5 \times 10^{-7} \frac{\text{gm}}{\text{cm}^2 \cdot \text{min}}$) with a thermal expansion of $178 \times 10^{-7} / ^\circ\text{C}^{-1}$ which matches the thermal expansion of copper and 304 stainless steel alloys. We believe that future work will yield phosphate glass ceramics which have corrosion resistance to aqueous attack comparable to the typical silicate sealing glasses. This development is currently being done, and a study is in progress to further define the corrosion mechanism in phosphate glass ceramics.

V. APPLICATIONS

Several applications for phosphate glass ceramics are summarized in this section.

Copper and aluminum alloys have been considered for use in vacuum tubes. Aluminum alloys are desirable due to their ease of machinability and formability plus possessing low permeability to both hydrogen and helium gas. Selected copper alloys--including copper-titanium, copper-aluminum-silicon, and copper-chrome alloys, form oxide layers which are impermeable to hydrogen or helium gas and offer higher mechanical strength than aluminum alloys. The utilization of these high expansion alloys would greatly reduce stresses generated in encapsulated tubes due to thermal expansion mismatches between the tube materials and epoxy encapsulants.

This application would require high mechanical strength and low helium permeability in the glass ceramics. Helium permeabilities are among the lowest of any glasses available.^{1,10} As discussed earlier, the mechanical properties of the glasses improve with formation of crystal phases in the glass. Further improvement in mechanical properties is expected as additional control over the crystallization process is achieved.

A second group of applications will use copper, stainless steel, or aluminum pins sealed in aluminum casings. This technology requires a glass ceramic material with a thermal expansion coefficient equal to that of the metal pins which will seal to both pin and aluminum casing. If aluminum pins are used, resulting in matched expansion coefficients of the materials, then stress-free

seals are obtained. If copper or steel pins are used, compressive stresses are generated on the glass ceramic surface at the ceramic-casing interface.

Relevant properties of these pin seals which must be examined for weapon applications include: seal strength, electrical breakdown between pin and casing, mechanical shock and vibration, thermal shock, humidity effects, and degree of thermal cycling possible without degrading seal integrity. Seals with copper and steel pins are currently under test. The seal processes and test results will be the subject of a subsequent report.

Potential pin seal applications include using aluminum alloys to replace steel casings in selected cable connectors to achieve weight reduction. Electrical feed through into lightweight aluminum casings in various controllers is also desirable. Lower cost hermetic seals may result because aluminum is readily available and easily fabricated.

VI. SUMMARY

We have developed glass ceramics based on the $\text{Na}_2\text{O} \cdot \text{CaO} \cdot \text{P}_2\text{O}_5$ and $\text{Na}_2\text{O} \cdot \text{BaO} \cdot \text{P}_2\text{O}_5$ glass system. Compositional and/or crystallization schedule adjustments allow formation of glass ceramics with thermal expansion coefficients equal to copper, 300 series steels, or aluminum alloys. Initial results indicate fracture toughness can be increased by 30 to 40% in the glass ceramics compared to the glass. We expect future studies to further enhance the mechanical properties.

We believe that these new insulator materials will extend the materials choices and combinations available to the design organization and could result in lower cost hermetic devices.

VII. ACKNOWLEDGEMENTS

The author acknowledges the assistance of Harold Gough and Sandy Lappin for sample preparation and property measurements and Elsie Kling (GENDD) for the X-ray diffraction analyses.

VIII. REFERENCES

1. J. A. Wilder, Jr., "Development of High Thermal Expansion Glasses for Sealing to Aluminum Alloys, I," SAND78-1694 (November 1978).
2. I. Gutzow, S. Toshev, M. Marinov, and E. Popov, "Nucleation and Crystal Growth in a Model Glass Initiated by Noble Metal Particles," Proc. 9th Conf. Silicate Ind., Budapest 65-72 (1968).
3. G. E. Rindone and R. J. Ryder, "Phase Separation Induced by Platinum in Sodium Phosphate Melts," Glass Ind. 29-31 + 51, (January, 1957).
4. Warren R. Beck, "Crystallographic Inversions of the Aluminum Orthophosphate Polymorphs and Their Relation to Those of Silica," J. Amer. Ceram. Soc., 32 (4), 147-151 (1949).
5. F. A. Hummel, "Properties of Some Substances Isostructural with Silica," J. Amer. Ceram. Soc., 32 (10), 320-326 (1949).
6. T. Miriya, Y. Akau, and N. Natano, "Devitrification Process in $\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$ Family Glasses," Yogyo Kyokai Shi, 68, 145-153 (1960).
7. J. F. MacDowell and L. E. Wilson, " $\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot \text{B}_2\text{O}_3$ Glass-Ceramic Articles and Methods," U.S. Patent 3,519,445, July 7, 1970.
8. R. M. Klein, A. G. Kolbeck, and C. L. Quackenbush, "Glass Formation and Properties in the Aluminum Borophosphate System," Ceramic Bulletin, 57 (2), 199-202 and 215-216 (1978).
9. J. J. Brown and F. A. Hummel, "Dilatometric and X-ray Data for Zinc Compounds, II. Phosphates and Vanadates," Trans. Brit. Ceram. Soc., 64 (1965).
10. J. E. Shelby and J. A. Wilder, Jr., "Helium Migration in Phosphate Glasses for Vacuum Tube Applications," SAND79-8214 (July 1979).
11. D. G. Holloway, "The Physical Properties of Glass," Wykeham Publications, London (1973).
12. T. Minami and J. D. Mackenzie, "Thermal Expansion and Chemical Durability of Phosphate Glasses," J. Amer. Ceram. Soc., 60 (5-6), 232-235 (1977).
13. P. W. McMillan, "Glass Ceramics," 2nd Edition, Academic Press, London (1979).
14. L. M. Barker, "Short Rod K_{IC} Measurements of Al_2O_3 ," presented at International Symposium on Fracture Mechanics, Penn State University, July 27-29, 1977.

TABLE 1

Variation in Thermal Expansion Coefficients of
Glass Ceramics as a Function of Parent Glass
Composition and Heat Treatment Schedules

<u>PARENT Glass Composition (Mole%)</u>	<u>Nucleation Temperature (°C) and Time (Hours)</u>	<u>Growth Temperature (°C) and Time (Hours)</u>	<u>$\alpha \times 10^7 (^\circ\text{C}^{-1})$</u>
40Na ₂ O·10BaO·50P ₂ O ₅	400°C at 2 Hours	450°C at 2 Hours	225
40Na ₂ O·10BaO·50P ₂ O ₅	450°C at 2 Hours	500°C at 2 Hours	224
40Na ₂ O·10CaO·50P ₂ O ₅	400°C at 2 Hours	450°C at 2 Hours	224
40Na ₂ O·10CaO·50P ₂ O ₅	450°C at 2 Hours	500°C at 2 Hours	196
30Na ₂ O·20BaO·50P ₂ O ₅	400°C at 2 Hours	450°C at 2 Hours	204
30Na ₂ O·20BaO·50P ₂ O ₅	450°C at 2 Hours	500°C at 2 Hours	203
30Na ₂ O·20CaO·50P ₂ O ₅	400°C at 2 Hours	450°C at 2 Hours	170
20Na ₂ O·30BaO·50P ₂ O ₅	400°C at 2 Hours	450°C at 2 Hours	170
20Na ₂ O·30BaO·50P ₂ O ₅	450°C at 2 Hours	500°C at 2 Hours	162

NOTE: All glasses doped with .05 wt% Pt for nucleation.

TABLE 2

Variation in Fracture Toughness of Glass
Ceramics as a Function of Heat Treatment Schedules

Parent Glass Composition (mole%)				Crystallization Cycle	$\alpha \times 10^7$ (Cerammed)	K_{IC} (MPa $\sqrt{m}$)
Na ₂ O	BaO	Al ₂ O ₃	P ₂ O ₅			
40	10	0	50	1 hr. @ 330°C 2 hr. @ 360°C 2 hr. @ 390°C	225	.41
"	"	"	"	1 hr. @ 330°C 2 hr. @ 360°C 12 hr. @ 390°C	225	.51
40	10	1	49	2 hr. @ 400°C 2 hr. @ 450°C	225	.47
"	"	"	"	2 hr. @ 400°C 12 hr. @ 450°C	219	.44
40	10	3	47	2 hr. @ 400°C 2 hr. @ 450°C	208	.50
"	"	"	"	2 hr. @ 400°C 12 hr. @ 450°C	211	.65

K_{IC} of amorphous SiO₂ $\approx$.74 MPa $\sqrt{m}$.

TABLE 3

LEACH RATE DATA FOR GLASS CERAMIC MATERIALS IN DEIONIZED WATER

Parent Composition (mol %)*	Crystallization Cycle	Leaching Bath Temp (°C)	Leach** Rate	Sample Appearance After Leaching
40Na ₂ O·10BaO·1Al ₂ O ₃ ·49P ₂ O ₅	400°C @ 2 hr. + 450°C @ 2 hr.	20°	5.4×10^{-5}	Pitted, crumbly
		70°	6.2×10^{-5}	Reduced to powder
40Na ₂ O·10BaO·2Al ₂ O ₃ ·48P ₂ O ₅	400°C @ 2 hr. + 450°C @ 2 hr.	20°	5.6×10^{-5}	Pitted
		70°	6.2×10^{-5}	Pitted, crumbly
40Na ₂ O·10BaO·3Al ₂ O ₃ ·47P ₂ O ₅	400°C @ 2 hr. + 450°C @ 2 hr.	20°	8.0×10^{-6}	Slight pitting; limited attack
		70°	5.0×10^{-5}	Pitted surface
30Na ₂ O·20BaO·3Al ₂ O ₃ ·47P ₂ O ₅	450°C @ 2 hr. + 500°C @ 2 hr.	20°	1.8×10^{-5}	Pitted, flaky surface
		70°	4.7×10^{-5}	Pitted, flaky surface
27Na ₂ O·20BaO·3Al ₂ O ₃ ·55P ₂ O ₅	450°C @ 1 hr. + 520°C @ 2 hr.	25°	5.0×10^{-7}	Good structural integrity
		71°	9.2×10^{-6}	Slight pitting; limited attack
29Na ₂ O·21BaO·3Al ₂ O ₃ ·47P ₂ O ₅	500°C @ 15 min.	21°	4.9×10^{-5}	Slight pitting of surface
		70°	2.1×10^{-5}	Pitted, crumbly

* All glass ceramics doped with 0.03 wt% Pt

** Units of gm/cm²·min.Leach rate of a soda-lime window glass 5×10^{-8} gm/cm²·min. at 20°C

Figure 1. Change in length versus temperature for cristobalite SiO_2 and the cristobalite form of AlPO_4 (Fig. 5 of Ref. 5).

Figure 2. Schematic illustration of temperature versus time cycle for controlled crystallization of glasses.

Figure 3. Thermal expansion coefficients of glass ceramic materials versus thermal expansion coefficients of parent glasses.

Figure 4. Thermal expansion coefficients of glass ceramic materials in the Na₂O·BaO·P₂O₅ system versus thermal expansion coefficient ranges for aluminum, copper, and steel alloys.

DISTRIBUTION

M. F. Dilmore
General Electric
Neutron Devices Department
P. O. Box 11508
St. Petersburg, FL 33733

I. L. Levine
General Electric
Neutron Devices Department
P. O. Box 11508
St. Petersburg, FL 33733

R. H. Bristow
General Electric
Neutron Devices Department
P. O. Box 11508
St. Petersburg, FL 33733

1471-4 R. D. Snidow
1471-4 D. Stewart
1471-4 H. McCollister
2154 J. P. Brainard
2154 F. X. Daut
2154 R. O. Work
2350 J. T. Grissom
2354 B. E. Barnaby
2354 G. J. Kominiak
3141 T. L. Werner (3)
3151 W. L. Garner (3)
3152-3 R. P. Campbell (25)
for DOE/TIC
5800 R. S. Claassen
Attn: 5810 R. G. Kepler
5820 R. E. Whan
5830 M. J. Davis
5822 E. J. Graeber
5822 C. R. Hills
5840 N. J. Magnani
5845 R. J. Eagan
5845 J. A. Wilder, Jr. (4)
5845 S. M. Lappin
8110 J. F. Barham, Jr.
8150 J. L. Wirth
8160 R. D. Cozine
8266 E. A. Aas
8310 D. M. Schuster
8342 J. Shelby

[illegible]