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**OAK RIDGE
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MARTIN MARIETTA

**DEVELOPMENT OF
LOW-EXPANSION CERAMICS
WITH STRENGTH RETENTION
TO ELEVATED TEMPERATURES**

FINAL REPORT

D. A. Hirschfeld
J. J. Brown, Jr.

CERAMIC TECHNOLOGY PROJECT

MANAGED BY
MARTIN MARIETTA ENERGY*SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

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DEVELOPMENT OF LOW-EXPANSION CERAMICS FOR DIESEL ENGINE APPLICATIONS

D. A. Hirschfeld and J. J. Brown, Jr.

ABSTRACT

The development of advanced engines has resulted in the need for new ceramic compositions which exhibit thermo-mechanical properties suitable for the engine environment, e.g., low thermal expansion, stability to 1200°C, and thermal shock resistance. To meet these goals, a two phase research program was instituted. In the first phase, new oxide ceramics were identified in the AlPO_4 - β -eucryptite, β -cristobalite, mullite and zircon systems. This research focused on screening and property characterization of ceramics in the four systems. The most promising compositions in the AlPO_4 - β -eucryptite and zircon systems were then further evaluated and developed in the second phase with the goal of being ready for prototype testing in actual engines. Of the compositions, calcium magnesium zirconium phosphate (zircon system) exhibits the most desirable properties and is presently being developed for commercialization.

PREFACE

This investigation was initiated in 1986 in an attempt to identify new low-expanding oxide phases that might have potential as ceramic components in advanced heat engines. The results reported here provided the basis for five Masters of Science theses, four Ph.D. theses, and three patents.

Jay Tu (M.S.) investigated the mullite systems, Jinmin Kim (Ph.D.) the NZP systems, and Tawei Sun (Ph.D.) the stabilized β -cristobalite phases. K. H. Lee (Ph.D.) and Laurent Battu (M.S.) examined in situ whisker reinforced modified β -eucryptite. S. M. VanAken studied CMZP and James Liu (M.S.) lightweight CMZP. All of these students have completed their graduate programs. Students in the final stages of completing their advanced degrees are Yaping Yang (Ph.D.) and William Russ (M.S.).

The patents issued as a result of this work are: (1) Ceramic Materials with Low Thermal Conductivity and Low Coefficients of Thermal Expansion, (2) An In-Situ Whisker Reinforced Glass-Ceramic, (3) Alkali Corrosion Resistance Coatings and Ceramic Foams Having Superfine Open Cell Structure and Method of Processing.

PART I - IDENTIFICATION OF NEW LOW EXPANSION OXIDES

INTRODUCTION

The need for stable fabricable low thermal expansion ceramics for use in advanced heat engines was first recognized in the Department of Energy Advanced Gas Turbine (AGT) technology programs. More recently, the need for ceramic materials having low thermal expansion for use in components of advanced low heat rejection diesel engines has also been recognized. Components for the AGT, including the regenerator and other parts in the hot flow path, operate under thermal cyclic or other conditions which require low thermal expansion in order for the components to have satisfactory service life. Only two major ceramic systems--magnesia-alumina-silica and the lithia-alumina-silica--have been evaluated extensively for use in fabricating these low expansion ceramic components. Compositions evaluated extensively in the magnesia-alumina-silica system are near the composition of the compound cordierite, whereas compositions evaluated in the lithia-alumina-silica system are near that of the compound spodumene. Advanced low heat rejection diesel engine designs also have demonstrated the need for low thermal expansion ceramics which also have relatively high mechanical strength. Ceramic materials based upon either spodumene or cordierite have relatively low strength and high thermal expansion compared to fused silica, for example. It is of considerable importance to determine whether other ceramic systems exist in which the thermal expansion can be tailored so as to be very near zero over a relatively wide temperature range, extending to at least 1200°C.

The research herein includes (1) synthesis, (2) property characterization, and (3) fabrication of candidate low thermal expansion ceramics from four systems based upon aluminum phosphate, silica, mullite, and zircon. In the first

two systems, the goal is to stabilize low thermal expansion, high temperature, high crystal symmetry phases via solid solution formation. In mullite, deviation from stoichiometry and solid solution formation are utilized to reduce the thermal expansion. In zircon, the crystal anisotropy and thermal expansion are reduced via solid solution formation. Based upon earlier data of the investigators, compositional ranges are evaluated by fabricating experimental specimens and determining phase content plus microstructure, thermal expansion, solidus temperature, and density. Those compositions which exhibit acceptable sintering, phase composition, and expansion characteristics are studied in more detail, including flexural strength, thermal conductivity, and crystal structure.

AlPO₄-β-EUCRYPTITE SYSTEM

A system composed of AlPO₄, BPO₄, and Li₂O•Al₂O₃•2SiO₂ (β-eucryptite) was evaluated for potential ultra-low expansion. Aluminum phosphate and BPO₄ are half-breed derivatives of SiO₂ with either Al³⁺, B³⁺, or P⁵⁺ substituting for Si⁴⁺ in silica. β-eucryptite has an overall negative coefficient of expansion up to 1000°C. Addition of SiO₂ in solid solution brings the coefficient closer to zero. For example, the coefficient of thermal expansion of a solid solution of 50% AlPO₄ and 50% β-eucryptite is as low as fused silica.

Even though a significant difference exists in the ionic radii of Al³⁺ and B³⁺, the compounds AlPO₄ and BPO₄ form a continuous solid solution above 1200°C. This is possible since both compounds exhibit an ordered, tetragonal, high cristobalite structure at this temperature. This solid solution can be quenched in a metastable form to room temperature. The stabilization of this β-cristobalite solid solution is chemical. Long term heat treatments can cause exsolution resulting in the appearance of Al(PO₃)₃ due to the volatility of B₂O₃ and P₂O₅.

Compositions in the system BPO₄-AlPO₄ in the range of 10-70 mol% AlPO₄ were studied by forming a glass followed by recrystallization. Solid-state reactions between Li₂CO₃, Al₂O₃, and Potter's flint have been used to form β-eucryptite. The ternary phase equilibria between AlPO₄, BPO₄, and β-eucryptite were studied by first mapping the binary phase diagrams and then AlPO₄-β-

eucryptite was selected the most promising candidate for further evaluation.

Solid solutions of β -eucryptite ($\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) with AlPO_4 were studied in an effort to stabilize the high temperature polymorphs such as β -cristobalite. The work has focused on high AlPO_4 -content solid solution formation between AlPO_4 and β - LiAlSiO_4 , and elemental substitution in some of the solid solutions.

Samples were prepared by either solid-state reaction or sol-gel techniques. Raw materials included silicic acid, $\text{Al}(\text{OH})_3 \cdot n\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{HPO}_4$ or $\text{NH}_4\text{H}_2\text{PO}_4$, Li_2CO_3 , MgCO_3 , TiO_2 , GeO_2 , $\text{Si}(\text{OC}_2\text{H}_5)_4$, $(\text{C}_2\text{H}_5\text{O})_3\text{P}(\text{O})$, $[(\text{CH}_3)_2\text{CHO}]_3\text{Al}$, and $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$. XRD and petrographic phase identifications were made on the resulting sample powders. Single phase samples were pressed into bars and sintered at the desired temperature for subsequent thermal expansion measurements. Linear thermal expansion was measured from room temperature to 1000°C with an automatic dual push rod dilatometer; axial thermal expansion to 1100°C was measured by high temperature XRD using platinum powder as an internal standard. Scanning rate was $2^\circ/\text{min}$ in a 2θ range of 19° to 50° . Three major reflections, (100), (102), and (114), were used. Phase stability of specimens was studied by differential thermal analysis (DTA) with a Perkin-Elmer thermal analysis system 7/4 ($20^\circ\text{C}/\text{min}$ heating rate to 1300, 1400, and 1500°C). Thermal shock tests for compositions having low thermal expansion were conducted by quenching bars from progressively higher temperatures into water of room temperature until cracking was observed. For retained flexural strength, or modulus of rupture (MOR) measurements, more than 20 rectangular specimens were pressed and sintered from the sample powders for each of the compositions exhibiting low thermal expansion. The 4-point bend method was used for these measurements. For each composition, 10 specimens were tested as originally formed; others were tested after undergoing different thermal shock cycles. At least 3 specimens were tested for each condition.

β - LiAlSiO_4 - AlPO_4 System and Elemental Substitution

The possibility of forming solid solution between β - LiAlSiO_4 and AlPO_4 within the AlPO_4 content range of 56-90 mol% was studied. Sample

composition, processing, phase analysis, and thermal expansion details are summarized in Table 1. Samples 1-5 were prepared by solid-state reaction and fired at 1200°C or higher for more than 100 hours to achieve equilibrium. XRD phase identification revealed the presence of more than one phase in all samples after the heat treatments. It is likely that a single phase solid solution cannot form within this AlPO_4 range.

The effects of SiO_2 content in $\beta\text{-LiAlSiO}_4\text{-AlPO}_4$ solid solution on thermal expansion behavior of compositions were further studied. With an increased SiO_2 content in the compositions $\text{Li}_{0.5}\text{AlP}_{0.5}\text{Si}_{0.5}\text{O}_4$, $\text{Li}_{0.5}\text{AlP}_{0.5}\text{Si}_{0.6}\text{O}_{4.2}$, and $\text{Li}_{0.5}\text{AlP}_{0.5}\text{Si}_{0.7}\text{O}_{4.4}$, (samples 6-8 in Table 1), the average CTE (30-1000°C) decreased from $-10.3 \times 10^{-7}/^\circ\text{C}$ to $-11.9 \times 10^{-7}/^\circ\text{C}$ to $-15.6 \times 10^{-7}/^\circ\text{C}$, respectively. The results were similar in the case of compositions $\text{Li}_{0.48}\text{AlP}_{0.52}\text{Si}_{0.48}\text{O}_{0.4}$, $\text{Li}_{0.48}\text{AlP}_{0.52}\text{Si}_{0.576}\text{O}_{4.192}$, and $\text{Li}_{0.48}\text{AlP}_{0.52}\text{Si}_{0.672}\text{O}_{4.384}$ (samples 9-11 in Table 1), where the CTE decreased from $-7.6 \times 10^{-7}/^\circ\text{C}$ to $-10.5 \times 10^{-7}/^\circ\text{C}$ to $-12.9 \times 10^{-7}/^\circ\text{C}$, respectively. It appears that an increase in SiO_2 content increases the negative thermal expansion of $\beta\text{-LiAlSiO}_4\text{-AlPO}_4$ solid solution.

Work has continued on the effect of the substitution of Mg^{2+} ions for Li^+ ions in $\beta\text{-LiAlSiO}_4\text{-AlPO}_4$ solid solutions. As shown in Table 1, compositions $\text{Mg}_{0.01}\text{Li}_{0.46}\text{AlP}_{0.52}\text{Si}_{0.48}\text{O}_4$ (sample 12), $\text{Mg}_{0.02}\text{Li}_{0.44}\text{AlP}_{0.52}\text{Si}_{0.48}\text{O}_4$ (sample 13), $\text{Mg}_{0.03}\text{Li}_{0.42}\text{AlP}_{0.52}\text{Si}_{0.48}\text{O}_4$ (sample 14), $\text{Mg}_{0.035}\text{Li}_{0.41}\text{AlP}_{0.52}\text{Si}_{0.48}\text{O}_4$ (sample 16), and $\text{Mg}_{0.04}\text{Li}_{0.4}\text{AlP}_{0.52}\text{Si}_{0.48}\text{O}_4$ (sample 15), prepared by solid-state reaction, exhibited single phases and decreasing negative expansion (30-1000°C) with increasing Mg^{2+} content. $\text{Mg}_{0.05}\text{Li}_{0.38}\text{AlP}_{0.52}\text{Si}_{0.48}\text{O}_4$ (sample 17, 20 mol% of Li^+ replaced by Mg^{2+}) was multiphase after heat treatment, indicating that although the substitution of Mg^{2+} for Li^+ may lower the negative expansion of the material, the maximum replaceable amount of Li^+ by Mg^{2+} in this system appears to be about 20 mol%.

The ion substitutions of $\text{Ti}^{4+} = \text{Al}^{3+} + \text{Li}^+$ or $\text{Ti}^{4+} = \text{Si}^{4+}$ and $\text{Ge}^{4+} = \text{Al}^{3+} + \text{Li}^+$ or $\text{Ge}^{4+} = \text{Si}^{4+}$ were studied. In an attempt to introduce the ion exchange of $\text{Ti}^{4+} = \text{Al}^{3+} + \text{Li}^+$, two samples having the composition of $\text{Li}_{0.45}\text{Al}_{0.95}\text{Ti}_{0.05}\text{P}_{0.5}\text{Si}_{0.5}\text{O}_4$ (samples 18-19) were prepared. Sample 18, processed via solid-state reaction, was fired 3 times at 1200°C (for 84, 48, and 40 hours) with powder grinding and mixing between each firing. Sample 19, processed using the sol-gel technique, was fired at 1200°C for 36 hours. Both final

Table 1. Sample Processing and Thermal Expansion Results for the AlPO_4 - β - LiAlSiO_4 System.

Sample No.	Initial Composition	Sample and Bar Processing Temp/Time($^{\circ}\text{C}/\text{h}$)	Phase Composition	Linear Thermal Expansion $\alpha(\times 10^{-7}/^{\circ}\text{C})$
1	$\text{Li}_{0.44}\text{AlP}_{0.56}\text{Si}_{0.44}\text{O}_4$	1210/48, 1200/63, 1200/36	M.P.	N.A.
2	$\text{Li}_{0.25}\text{AlP}_{0.75}\text{Si}_{0.25}\text{O}_4$	1200/58, 1250/35, 1300/24	M.P.	N.A.
3	$\text{Li}_{0.2}\text{AlP}_{0.8}\text{Si}_{0.2}\text{O}_4$	1200/58, 1250/35, 1300/24	M.P.	N.A.
4	$\text{Li}_{0.15}\text{AlP}_{0.8}\text{Si}_{0.2}\text{O}_4$	1200/58, 1250/35, 1300/24	M.P.	N.A.
5	$\text{Li}_{0.1}\text{AlP}_{0.9}\text{Si}_{0.2}\text{O}_4$	1200/58, 1250/35, 1300/24	M.P.	N.A.
6	$\text{Li}_{0.5}\text{AlP}_{0.5}\text{Si}_{0.5}\text{O}_4$	1200/72 Bar: 1200/10	S.S.	-10.3
7	$\text{Li}_{0.5}\text{AlP}_{0.5}\text{Si}_{0.6}\text{O}_{4.2}$	1200/53, 1200/36 Bar: 1200/10	S.S.	-11.9
8	$\text{Li}_{0.5}\text{AlP}_{0.5}\text{Si}_{0.7}\text{O}_{4.4}$	1200/53, 1200/36 Bar: 1200/10	S.S.	-15.6
9	$\text{Li}_{0.48}\text{AlP}_{0.52}\text{Si}_{0.48}\text{O}_4$	1200/72 Bar: 1200/10	S.S.	-7.6
10	$\text{Li}_{0.48}\text{AlP}_{0.52}\text{Si}_{0.576}\text{O}_{4.192}$	1200/53, 1200/36 Bar: 1200/10	S.S.	-10.5
11	$\text{Li}_{0.48}\text{AlP}_{0.52}\text{Si}_{0.672}\text{O}_{4.384}$	1200/53, 1200/36 Bar: 1200/10	S.S.	-12.9
12	$\text{Mg}_{0.01}\text{Li}_{0.46}\text{AlP}_{0.52}\text{Si}_{0.48}\text{O}_4$	1200/72, 1200/44 Bar: 1200/10	S.S.	-3.8

13	$\text{Mg}_{0.02}\text{Li}_{0.44}\text{AlP}_{0.52}\text{Si}_{0.48}\text{O}_4$	1200/72,1200/44 Bar: 1200/10	S.S.	-3.1
14	$\text{Mg}_{0.03}\text{Li}_{0.42}\text{AlP}_{0.52}\text{Si}_{0.48}\text{O}_4$	1200/72,1200/44 Bar:1200/10	S.S.	-2.6
15	$\text{Mg}_{0.04}\text{Li}_{0.4}\text{AlP}_{0.52}\text{Si}_{0.48}\text{O}_4$	1200/72,1200/44 Bar: 1200/10	S.S.	-2.0
16	$\text{Mg}_{0.035}\text{Li}_{0.41}\text{AlP}_{0.52}\text{Si}_{0.48}\text{O}_4$	1200/84,1200/36	S.S.	-2.3
17	$\text{Mg}_{0.05}\text{Li}_{0.38}\text{AlP}_{0.52}\text{Si}_{0.48}\text{O}_4$	1200/54,1200/60 1200/74	M.P.	N.A.
18	$\text{Li}_{0.45}\text{Al}_{0.95}\text{Ti}_{0.05}\text{P}_{0.5}\text{Si}_{0.5}\text{O}_4$	1200/84,1200/48 1200/40	S.S. with Rutile	N.A.
19	$\text{Li}_{0.45}\text{Al}_{0.95}\text{Ti}_{0.05}\text{P}_{0.5}\text{Si}_{0.5}\text{O}_4$	Sol-gel;1200/36	S.S. with Rutile	N.A.
20	$\text{Li}_{0.4}\text{Al}_{0.9}\text{Ti}_{0.1}\text{P}_{0.5}\text{Si}_{0.5}\text{O}_4$	1200/84,1200/60 1200/36	S.S. with Rutile	N.A.
21	$\text{Li}_{0.4}\text{AlP}_{0.5}\text{Si}_{0.45}\text{Ti}_{0.05}\text{O}_4$	1200/48 (melted) 1180/48	Multiphase	N.A.
22	$\text{Li}_{0.42}\text{Al}_{0.95}\text{Ge}_{0.05}\text{P}_{0.52}\text{Si}_{0.48}\text{O}_4$	1180/48,1190/36 1205/25	S.S. with small amount of AlPO_4	-10.4
23	$\text{Li}_{0.48}\text{AlP}_{0.52}\text{Si}_{0.24}\text{Ge}_{0.24}\text{O}_4$	1180/48 1190/36(melted) 1170/30	Multiphase	N.A.
24	$\text{Li}_{0.48}\text{AlP}_{0.52}\text{Si}_{0.32}\text{Ge}_{0.16}\text{O}_4$	1180/48,1170/30 1180/30	S.S. with small amount of AlPO_4	N.A.
25	$\text{Li}_{0.48}\text{AlP}_{0.52}\text{Si}_{0.40}\text{Ge}_{0.08}\text{O}_4$	1180/48,1170/28	S.S.	-2.5

M.P. = More than one phase.

S.S. = β - LiAlSiO_4 Solid solution.

N.A. = Not available.

samples had a phase composition of β -LiAlSiO₄ solid solution with a small amount of rutile. In the cases of (Li_{0.4}Al_{0.9}Ti_{0.1})P_{0.5}Si_{0.5}O₄ (sample 20) and Li_{0.5}AlP_{0.5}(Si_{0.45}Ti_{0.05})O₄ (sample 21), second phases were present after the heat treatment. It is likely that, due to its larger size, Ti⁴⁺ cannot easily enter the 4-coordinated position to replace either the Al³⁺ or Si⁴⁺ in the solid solution.

In (Li_{0.42}Al_{0.95}Ge_{0.05})P_{0.52}Si_{0.48}O₄ (sample 22), Ge⁴⁺ was initially introduced to replace Al³⁺ and Li⁺. In Li_{0.48}AlP_{0.52}(Si_{0.32}Ge_{0.16})O₄ (sample 24) and Li_{0.48}AlP_{0.52}(Si_{0.24}Ge_{0.24})O₄ (sample 23), Ge⁴⁺ was introduced to replace Si⁴⁺. All three compositions formed second phases after heat treatment. However, with a decreased Ge⁴⁺ substitution for Si⁴⁺ in Li_{0.48}AlP_{0.52}(Si_{0.4}Ge_{0.08})O₄ (about 16.7 mol% Si⁴⁺ was substituted by Ge⁴⁺, sample 25), single phase β -LiAlSiO₄ solid solution was formed. This composition exhibited an average CTE value of $-2.5 \times 10^{-7}/^{\circ}\text{C}$ from 30 to 1000°C, a substantial reduction in negative thermal expansion when compared to Li_{0.48}AlP_{0.52}Si_{0.48}O₄ ($-7.6 \times 10^{-7}/^{\circ}\text{C}$).

DTA Results

Compositions showing a single phase by XRD were analyzed by DTA to evaluate the thermal stability and the effects of composition change on melting behavior. Peaks corresponding to phase transformation were not observed for any of the samples analyzed.

The DTA results shown in Table 2 indicate that the melting point of β -LiAlSiO₄-AlPO₄ solid solution increased with AlPO₄ content. This is illustrated by compositions in which the AlPO₄ content increases from 50 to 54 mol% (compositions 2,4,5). The melting point of the solid solution appears to increase with increased SiO₂ content, as illustrated by the first three compositions in Table 2. Partial substitution of Mg²⁺ for Li⁺ (composition 7) and Ge⁴⁺ for Si⁴⁺ (composition 9) appeared to lower the melting temperature when compared to the identical composition without substitutions (composition 4).

Axial Thermal Expansion Results

The axial thermal expansion behavior of Li_{0.5}AlP_{0.5}Si_{0.465}O_{3.93} and Li_{0.41}Mg_{0.035}AlP_{0.52}Si_{0.48}O₄ is shown in Figures 1 and 2. The former had an

Table 2. DTA Results of Single Phase Compositions.

Composition	Maximum temperature reached ($^{\circ}\text{C}$) ^a	Results
1. $\text{Li}_{0.5}\text{AlP}_{0.5}\text{Si}_{0.465}\text{O}_{0.393}$	1300	O.T.P. ^b ~ 1205 $^{\circ}\text{C}$
2. $\text{Li}_{0.5}\text{AlP}_{0.5}\text{Si}_{0.5}\text{O}_4$	1300	O.T.P. ~ 1213 $^{\circ}\text{C}$
3. $\text{Li}_{0.5}\text{AlP}_{0.5}\text{Si}_{0.6}\text{O}_{4.2}$	1400	O.T.P. ~ 1241 $^{\circ}\text{C}$
4. $\text{Li}_{0.48}\text{AlP}_{0.52}\text{Si}_{0.48}\text{O}_4$	1500	O.T.P. ~ 1222 $^{\circ}\text{C}$
5. $\text{Li}_{0.46}\text{AlP}_{0.54}\text{Si}_{0.46}\text{O}_4$	1400	O.T.P. ~ 1246 $^{\circ}\text{C}$
6. $(\text{Li}_{0.46}\text{Mg}_{0.01})\text{AlP}_{0.52}\text{Si}_{0.48}\text{O}_4$	1300	O.T.P. ~ 1218 $^{\circ}\text{C}$
7. $(\text{Li}_{0.41}\text{Mg}_{0.035})\text{AlP}_{0.52}\text{Si}_{0.48}\text{O}_4$	1300	O.T.P. ~ 1210 $^{\circ}\text{C}$
8. $(\text{Li}_{0.4}\text{Mg}_{0.04})\text{AlP}_{0.52}\text{Si}_{0.48}\text{O}_4$	1300	O.T.P. ~ 1208 $^{\circ}\text{C}$
9. $\text{Li}_{0.48}\text{AlP}_{0.52}(\text{Si}_{0.4}\text{Ge}_{0.08})\text{O}_4$	1300	O.T.P. ~ 1175 $^{\circ}\text{C}$

^a Heating rate = 20 $^{\circ}\text{C}/\text{min}$.^b O.T.P. = Onset temperature point on melting peak of DTA curve.

Figure 1. Axial expansion of $\text{Li}_{0.5}\text{AlP}_{0.5}\text{Si}_{0.465}\text{O}_{3.93}$.

Figure 2. Axial expansion of $\text{Li}_{0.41}\text{Mg}_{0.035}\text{AlP}_{0.52}\text{Si}_{0.48}\text{O}_4$.

average CTE value of $-0.56 \times 10^{-7}/^{\circ}\text{C}$ (30-1000 $^{\circ}\text{C}$); the latter had an average CTE value of $-2.3 \times 10^{-7}/^{\circ}\text{C}$ (30-1000 $^{\circ}\text{C}$). The expansions are anisotropic, but compared with pure $\beta\text{-LiAlSiO}_4\text{-AlPO}_4$, are much lower.

The average bulk CTE value, calculated on the basis of the axial thermal expansion results, for $\text{Li}_{0.5}\text{AlP}_{0.5}\text{Si}_{0.465}\text{O}_{3.93}$ is $-17.7 \times 10^{-7}/^{\circ}\text{C}$ and for $\text{Li}_{0.41}\text{Mg}_{0.035}\text{AlP}_{0.52}\text{Si}_{0.48}\text{O}_4$ is $-16 \times 10^{-7}/^{\circ}\text{C}$, both between 18 and 1100 $^{\circ}\text{C}$. The calculated CTE values are more negative than those measured by the dilatometer.

Thermal Shock Results

Thermal shock resistance and relative retained strength (normalized) were determined for the compositions $\text{Li}_{0.46}\text{AlP}_{0.54}\text{Si}_{0.465}\text{O}_4$, $\text{Li}_{0.5}\text{AlP}_{0.5}\text{Si}_{0.46}\text{O}_{3.93}$, and $\text{Li}_{0.41}\text{Mg}_{0.035}\text{AlP}_{0.52}\text{Si}_{0.48}\text{O}_4$. Results of these tests are summarized in Table 3. The decreasing negative thermal expansion for each composition studied was accompanied by an increase in the relative retained strength (MOR of specimens following 10 thermal shock cycles/MOR of specimens as-formed).

For the composition $\text{Li}_{0.46}\text{AlP}_{0.54}\text{Si}_{0.46}\text{O}_4$, the maximum temperature difference at which cracking was observed (ΔT_{max}) was 1150 $^{\circ}\text{C}$ (quenched from 1175 $^{\circ}\text{C}$ into water at 25 $^{\circ}\text{C}$). For the other two compositions quenched from 1200 $^{\circ}\text{C}$ into water at 25 $^{\circ}\text{C}$, no cracking was observed. Because 1200 $^{\circ}\text{C}$ was approaching the melting points of the compositions (see Table 2), quenching was not performed at higher temperatures.

The MOR values are plotted as a function of the number of thermal shock cycles in Figure 3. The results indicate that the MOR values of composition $\text{Li}_{0.41}\text{Mg}_{0.035}\text{AlP}_{0.52}\text{Si}_{0.48}\text{O}_4$ were lower than the MOR values of the other two compositions. Thus, the effect of $\text{Mg}^{2+} = \text{Li}^{+}$ ion exchange on the strength of the material should be investigated further.

Recrystallization

Generally, sample porosities in excess of 10% preclude the collection of any significant mechanical properties data. It is felt that the prime objective of the continuation of this research should be to develop the chemically-modified

Table 3. Results of Thermal Shock Experiments

Composition	Thermal Expansion (30-1000 °C) $\alpha (\times 10^{-7} / ^\circ\text{C})$	$\Delta T_{\text{max}} (^\circ\text{C})$	Relative retained strength* (%)
$\text{Li}_{0.46}\text{AlP}_{0.54}\text{Si}_{0.46}\text{O}_4$	-5.8	1150	39.3
$\text{Li}_{0.41}\text{Mg}_{0.035}\text{AlP}_{0.52}\text{Si}_{0.48}\text{O}_4$	-2.3	1175	46
$\text{Li}_{0.5}\text{AlP}_{0.5}\text{Si}_{0.465}\text{O}_{3.93}$	-0.96	1175	63.4

*(MOR of specimen after 10 thermal shock cycle/MOR of specimen as originally formed) $\times 100\%$.

Figure 3. MOR of thermally shocked specimens.

β -eucryptite- AlPO_4 compositions through processing, composition optimization, characterization, and parts fabrication to the point where they are attractive for testing in actual heat engines.

Because the β -eucryptite compositions are glass-forming and suitable for controlled recrystallization, this is likely to be the easiest and most economical process for densification. This task involves the addition of a suitable nucleation agent such as ZrO_2 or TiO_2 , forming glass, and optimizing the recrystallization heat treatment to yield maximum strength and/or toughness. Therefore, glass-ceramic forming techniques have been initiated for the composition $\text{Li}_{0.41}\text{Mg}_{0.035}\text{AlP}_{0.52}\text{Si}_{0.48}\text{O}_4$.

Preliminary batch compositions included the addition of 4 wt% ZrO_2 as a nucleation agent. A glass resulted from heat treating the raw materials [$\text{Al}(\text{OH})_3 \cdot n\text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$, Li_3CO_3 , MgSO_4 , silicic acid, and ZrO_2] at 1625°C for 24 h (heating rate of $70^\circ\text{C}/\text{min}$). Glass fragments obtained from this procedure are crystalline following a single heat treatment of 850°C for 48 h. XRD analyses of the recrystallized glass-ceramics showed the crystalline phases to be β -eucryptite solid solution with a trace amount of AlPO_4 .

It has recently been discovered that all previous β -eucryptite compositions formed by solid-state reaction contained about 10% Al_2O_3 as a second phase, along with trace amounts of AlPO_4 . It is likely that the undesirable phases resulted from heat treating an incompletely reacted solid solution phase. During heat treatment, AlPO_4 decomposed into Al_2O_3 and P_2O_5 . It, therefore, appears that to obtain the desired glass-ceramic phase composition, the raw materials must be fully reacted prior to glass-formation to form the AlPO_4 -free β -eucryptite solid solution phase.

Summary

1. Attempts to form a single phase solid solution between β - LiAlSiO_4 and AlPO_4 within the AlPO_4 content range of 55-90 mol% were unsuccessful. The limit of solid solubility was found to be 54 mol%.
2. SiO_2 content can change within a small range in the solid solutions without the structural changes. A decrease in SiO_2 content will reduce the

negative thermal expansion and, on the other hand, decrease the melting temperature of the solid solutions.

3. About 20 mol% of Li^+ can be substituted by Mg^{2+} in the solid solutions. This substitution can further decrease the negative thermal expansion and expansion anisotropy of the solid solutions. On the other hand, this substitution decreases the melting temperature and may lower the strength of the solid solutions.

4. Due to its large size, Ti^{4+} could not be introduced into 4-coordinated positions to replace Al^{3+} or Si^{4+} in the solid solutions.

5. Si^{4+} was substituted (up to about 16.7 mol%) by Ge^{4+} , leading to a decrease in the negative thermal expansion of the solid solution. Al^{3+} could not be substituted by Ge^{4+} in the solid solution.

β -CRISTOBALITE SYSTEM

Knowing that thermal expansion can be modified by forming a solid solution, and that the high temperature β -cristobalite (SiO_2) is most structurally and thermodynamically similar to fused silica, it is reasonable to choose silica as a matrix for developing new low thermal expansion ceramics. To do so, it is necessary to use compounds which are isostructural with silica and that will stabilize β -cristobalite down to room temperature. The compounds AlPO_4 , BPO_4 , and TiO_2 were evaluated for use as stabilizers. These additives only lowered the inversion temperature and did not stabilize the β -cristobalite.

By using compositions based on a framework silicate formula $\text{MO} \cdot \text{Al}_2\text{O}_3 \cdot \text{XSiO}_2$, where M represents divalent cations from alkaline earth and transition metals, β -cristobalite was stabilized. All the oxygen atoms in this structure are bridging oxygen and the M ions fit into the interstices to balance the charge.

β -cristobalite was successfully stabilized using sol-gel techniques. It was synthesized from both acid (HNO_3) and base (NH_4OH)-catalyzed solutions containing respective metal alkoxides and salts with a $\text{H}_2\text{O}/(\text{Al} + \text{Si})$ molar ratio ranging from 2 to 10. Upon the completion of hydrolysis and condensation reactions, the resultant gel was dried between 60 and 70°C to remove alcohol and H_2O , followed by heat treatment at 1000°C for 24 hours. XRD analysis

indicates that β -cristobalite was formed in compositions containing Ca, Sr, and Cu under base-catalyzed conditions, whereas amorphous phase was present as the dominating phase in all the acid-catalyzed samples. Results from differential scanning calorimetry (DSC) studies further support the fact that β -cristobalite is stabilized since no inversion peak was detected after repeated thermal scanning as shown in Figure 4.

Synthesis Results

In the $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2$ series of compositions, the concentration of 5% ($\text{CaO} + \text{Al}_2\text{O}_3$) appears to be crucial in the phase formation because anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) was always formed in addition to β -cristobalite when the ($\text{CaO} + \text{Al}_2\text{O}_3$) content exceeded 5%. On the other hand, α -quartz or amorphous phase coexisted with β -cristobalite when the ($\text{CaO} + \text{Al}_2\text{O}_3$) content was less than 5%. Although β -cristobalite was the dominant phase for samples prepared from the $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2$ compositions, amorphous phase was also present regardless of the pH value and H_2O concentration. Single phase β -cristobalite was obtained only from the $\text{CuO} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2$ series of compositions as shown in the XRD patterns in Figure 5.

Structural Evolution

The structural evolution of β -cristobalite from the x-ray amorphous xerogels was examined from 200 to 1000°C using Fast Fourier Transform Infrared spectroscopy (FTIR) as shown in Figures 6 and 7 for the $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 30\text{SiO}_2$ and $\text{CuO} \cdot \text{Al}_2\text{O}_3 \cdot 30\text{SiO}_2$ compositions, respectively. The difference between α -cristobalite and β -cristobalite in FTIR spectra is the 620cm^{-1} absorption peak, which occurs in α -cristobalite only as shown in Figure 8. The absence of the 620cm^{-1} absorption peak in Figures 6 and 8 indicates that β -cristobalite was embodied in the local gel structure. In other words, the local structure in the xerogel is identical to the crystalline counterpart, except that long range order has not developed at the early stage. Progressive heat treatment at high temperatures extends the ordered region and reduces the

Figure 4. DSC analyses of Cu-stabilized β -cristobalite
(scanning rate of 20°C/min.)

Figure 5. XRD of the $\text{CuO} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2$ compositions.

Figure 6. FTIR spectra of the gel prepared from the $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 30\text{SiO}_2$ composition after successive heat treatments 200, 400, 600, 800, and 1000°C

Figure 7. FTIR spectra of the gel prepared from the $\text{CuO} \cdot \text{Al}_2\text{O}_3 \cdot 30\text{SiO}_2$ composition. The gel was heated at 200, 400, 600, 800, and 1000 °C successively

(a)

(b)

Figure 8. FTIR spectra for (a) α -cristobalite and (b) β -cristobalite

unreacted functional groups as the 1100cm^{-1} peak becomes narrower with increasing temperature. Prolonged heat treatment at 1000°C eventually brings about the complete crystallization of β -cristobalite. The formation of β -cristobalite at the temperature far below its stability region is attributed to the local structure developed in the gel.

Stability Test

A stability test of the stabilized β -cristobalite was performed by heating the $\text{CuO}\cdot\text{Al}_2\text{O}_3\cdot\text{XSiO}_2$ series of samples isothermally at 1250°C for 10 hours. The results shown in Table 4 indicate that almost half of the β -cristobalite phase transformed to α -cristobalite and no exsolution was observed. The destabilization of β -cristobalite is apparently related to grain growth at high temperature. In other words, β -cristobalite is stabilized by the formation of fine crystals resulting from sol-gel processing. The effect of grain size on the stability of β -cristobalite can be made clear by including the surface energy term in the total free energy. For β -cristobalite to be stable at all temperatures, the free energy of β -cristobalite (G_β) has to be smaller than the free energy of α -cristobalite (G_α); that is,

$$G_\alpha - G_\beta = (4/3)\pi r^3(F_\alpha - F_\beta) + 4\pi r^2(\gamma_\alpha - \gamma_\beta) > 0$$

where F denotes the chemical free energy and r and γ represent grain size and surface energy, respectively. It is reasonable to assume γ_α is greater than γ_β since surface energy decreases with increasing temperature. Therefore, there exists a critical radius $r_c = 3(\gamma_\alpha - \gamma_\beta)/(F_\beta - F_\alpha)$, below which β -cristobalite is always stable.

Thermal Expansion Behavior

Aggregate thermal expansion data for the Cu-stabilized β -cristobalite compositions exhibiting single phases are summarized in Table 5. In contrast to the anticipated results, the CTE value of the stabilized β -cristobalite remains high irrespective of the presence of phase transformation, implying that

considerable flexibility still exists in the structure. The axial thermal expansion measured from room temperature to 1000°C indicates that tilting of the Si-O-Si angle continues to dominate the thermal expansion of β -cristobalite, especially at low temperatures as shown in Figure 9 and Table 6. The presence of the interstitial cations appears to have little effect on restraining the bond angle. Similar results were obtained for substitutions made on the framework cations. The bond angle change may not be as evident when the high-low inversion of cristobalite is present. As a result, framework structures linked by bridging oxygen almost always exhibit high expansion, except when their thermal expansion is highly anisotropic as in the case of β -spodumene, β -eucryptite, β -quartz, and cordierite.

Summary

1. β -cristobalite single phase can be synthesized at greatly reduced temperatures and time using sol-gel processing.
2. The stabilization of β -cristobalite is attributed to the surface energy effect resulting from the formation of fine grains.
3. Tilting of the Si-O-Si bond angle at low temperatures accounts for the high thermal expansion of the stabilized β -cristobalite regardless of the presence of phase transformation.

MULLITE SYSTEM

Ceramics based on the mullite system were examined for potential use in advanced heat engines because of their low expansion, high strength, high stability, and relatively low cost. Of all compounds in the alumina-silica binary system, it is the only stable compound under normal atmospheric pressure. The composition of mullite varies in a narrow range from 71.8 to 77.3 wt% Al_2O_3 and has been used widely in refractories because of its high melting temperature (1790°C).

Mullite has a low CTE because the volumes of (AlO_4) and (SiO_4) tetrahedra show little or no change with temperature due to their high bond strength. With increasing $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratios, more Al^{3+} ions will enter tetrahedral

Table 4. Stability Test Results for the Cu-Stabilized β -Cristobalite Heated at 1250°C for 10 Hours

Composition	Phase	% of conversion
$\text{CuO} \cdot \text{Al}_2\text{O}_3 \cdot 30\text{SiO}_2$	α -, β -cristobalite	44.8
$\text{CuO} \cdot \text{Al}_2\text{O}_3 \cdot 40\text{SiO}_2$	α -, β -cristobalite	48.6
$\text{CuO} \cdot \text{Al}_2\text{O}_3 \cdot 50\text{SiO}_2$	α -, β -cristobalite	48.6
$\text{CuO} \cdot \text{Al}_2\text{O}_3 \cdot 60\text{SiO}_2$	α -, β -cristobalite	49.6

Table 5. CTE Data for Cu-Stabilized β -Cristobalite Compositions Synthesized by Sol-Gel Techniques

Composition	Phase	CTE β ($10^{-7}/^\circ\text{C}$)
$\text{CuO} \cdot \text{Al}_2\text{O}_3 \cdot 20\text{SiO}_2$	β -crist(ss), unknown	---
$\text{CuO} \cdot \text{Al}_2\text{O}_3 \cdot 30\text{SiO}_2$	β -crist(ss)	75
$\text{CuO} \cdot \text{Al}_2\text{O}_3 \cdot 40\text{SiO}_2$	β -crist(ss)	79
$\text{CuO} \cdot \text{Al}_2\text{O}_3 \cdot 50\text{SiO}_2$	β -crist(ss)	77
$\text{CuO} \cdot \text{Al}_2\text{O}_3 \cdot 60\text{SiO}_2$	β -crist(ss)	78

Table 6. Thermal Expansion of β -Cristobalite in Various Temperature Ranges

Temperature ($^\circ\text{C}$)	RT-200	200-400	400-600	600-800	800-1000
α ($10^{-7}/^\circ\text{C}$)	95	73	39	26	7.2

Figure 9. The axial thermal expansion of the Ca-stabilized β -cristobalite

sites. The stability of (AlO_4) is less than that of (SiO_4) , resulting in slightly weaker bonding in tetrahedral sites. However, the overall effect on thermal expansion depends on the bonding strength of (AlO_6) octahedral sites. It has the weakest bond strength in the structure of mullite and is the least suitable due to the edge-sharing.

To minimize the CTE, mullite can be chemically modified through ionic substitution. When using other oxides to substitute for Si^{4+} or Al^{3+} , the charge causes the number of oxygen vacancies to vary, and the ionic size determines which site between tetrahedra and octahedra the cation occupies. The latter, in fact, determines the coordination number of substituting cations. For the above reason, the modifiers evaluated were TiO_2 , B_2O_3 , CrPO_4 , P_2O_5 , Ga_2O_3 , WO_3 , and the half-breed SiO_2 compounds AlPO_4 , BPO_4 , GaPO_4 , BaSO_4 , AlAsO_4 , GaAsO_4 , and GeO_2 .

The incorporation of the foreign ions into the mullite solid solution depends on the heat treatment of the modifying species and its solubility. At high temperatures, there is increased disorder of the mullite tetrahedral sites making it easier to substitute an ion. Both sol-gel and solid-state reaction processes were used to prepare the synthetic mullite.

The materials used to make up the compounds, either pure oxides or synthesized by mixing the desired oxide powders using acetone, were heat treated in covered alumina crucibles according to the firing schedules shown in Table 7. Subsequent to each firing, the samples were removed from the furnace, thoroughly mixed, and analyzed using XRD to insure that the desired product had been synthesized.

The sol-gel process used metal alkoxides as starting materials and the procedure is detailed in Figure 10. The starting metal alkoxides were $\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{Al}[(\text{CH}_3)_2\text{CHO}]_3$, $\text{Al}[\text{C}_2\text{H}_5\text{CH}(\text{CH}_3)\text{O}]_3$, $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$, $\text{B}(\text{CH}_3\text{O})_3$, and $\text{P}[\text{O}(\text{CH}_3\text{O})_3]$. For the processing of the TiO_2 -modified mullite, an evaluation was made of the effects of the precursor solution pH value on powder morphology. It was found that a basic condition (pH 7-12) yielded small aggregated particles of a uniform size (1-5 μm).

The optimum sintering/reaction range was determined by examining several TiO_2 -modified mullite samples heated at different temperatures. XRD data showed that sintering at 1500-1600°C produced the least amount of

sites. The stability of (AlO_4) is less than that of (SiO_4) , resulting in slightly weaker bonding in tetrahedral sites. However, the overall effect on thermal expansion depends on the bonding strength of (AlO_6) octahedral sites. It has the weakest bond strength in the structure of mullite and is the least suitable due to the edge-sharing.

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[1] The pH value of the solutions is usually maintained at 7.

[2] Powders are examined by XRD.

Figure 10. Flow chart showing the sol-gel synthesis of chemically-modified mullite.

Table 7. Solid-State Synthesis of the Half-Breed SiO_2 Compounds

Compound	Starting materials	Heat treatment ($^{\circ}\text{C/hr}$)
AlPO_4	$\text{Al}(\text{OH})_3 \cdot n\text{H}_2\text{O} + 1.01(\text{NH}_4)_2\text{HPO}_4$	400/4 +800/10+1100/72
BPO_4	$\text{H}_3\text{BO}_3 + 1.01(\text{NH}_4)_2\text{HPO}_4$	400/4 +800/10+1050/72
CrPO_4	$\text{Cr}_2\text{O}_3 + 2.02(\text{NH}_4)_2\text{HPO}_4$	400/2 +600/10+1080/48
GaPO_4	$\text{Ga}_2\text{O}_3 + 2.02(\text{NH}_4)_2\text{HPO}_4$	400/2 +600/10+1080/48
BaAsO_4	$2\text{H}_3\text{BO}_3 + 1.01\text{As}_2\text{O}_3$	100/2 +200/16+400/8+600/8+700/8
AlAsO_4	$\text{Al}_2\text{O}_3 + 1.01\text{As}_2\text{O}_3$	200/16+400/8 +600/8+700/8+900/12
GaAsO_4	$\text{Ga}_2\text{O}_3 + 1.01\text{As}_2\text{O}_3$	200/16+400/8 +600/8+700/8+900/12

Al_2TiO_5 and the highest degree of mullite formation and thus was the chosen temperature range for this study. Above 1600°C , AlTiO_5 decomposes into Al_2O_3 plus rutile indicating that mullite changes above 1600°C to an aluminum-rich mullite.

Unit cell parameters of four Ti-modified mullites were determined using the multiple linear regression method. High temperature XRD with a Buehler furnace was used to determine the axial thermal expansion of the Ga-modified mullite. All specimens were examined under an optical polarizing microscope to qualitatively detect the presence of different phases after sintering.

The CTE values were determined using a Netzsch Dual Push Rod Dilatometer Model 402ED on bar specimens 100mm by 10mm by 10mm or 100mm by 25mm by 6mm pressed in a steel mold at 60 and 20 MPa, respectively.

TiO_2 -Mullite Solid Solutions

Compositions, heat treatments, phase analyses, and CTE values of TiO_2 -mullite solid solutions prepared by solid state reactions and sol-gel processing are summarized in Tables 8 and 9, respectively. The results indicate that both preparation techniques yielded the same final equilibrium phase.

At TiO_2 contents or 3 wt% or less, mullite solid solutions formed, whereas above 3 wt%, Al_2TiO_5 formed as a second phase. Accordingly, this indicates that the solid solubility limit of TiO_2 in mullite is approximately 3 wt%. It was noted that rutile appeared when the TiO_2 in mullite is approximately 3 wt%. It was noted that rutile appeared when the TiO_2 content was 4-6 wt% and the $\text{Al}_2\text{O}_3/\text{SiO}_2$ molar ratio was about 1.5. The CTE values decreased slightly from 5.2 to about $4.7 \times 10^{-6}/^\circ\text{C}$ at the solid solubility limit as shown in Figure 11. Above 3 wt% TiO_2 , Al_2TiO_5 appears as a second phase and the CTE values decrease significantly due to the presence of Al_2TiO_5 . Although mixtures of Al_2TiO_5 and mullite solid solutions have very low CTE values, they exhibit poor

Table 8. Summary of TiO_2 -Mullite Compositions Synthesized by Solid-State Reaction

Sample No.	Composition (wt%)			A/S	Sintering ($^{\circ}\text{C}/\text{h}$)	Phase(s) present	CTE($^{\circ}\text{C}\times 10^{-6}$) R.T.-1000 $^{\circ}\text{C}$
	Al_2O_3	SiO_2	TiO_2				
J-009	71.08	27.92	1.00	1.5	1600/6 + 1200/8	M ¹	4.8
J-010	70.36	27.64	2.00	1.5	1600/8 + 1200/8	M	4.9
J-011	69.64	27.36	3.00	1.5	1600/12 + 1200/19	M	4.7
J-012	68.92	27.08	4.00	1.5	1600/12 + 1200/19	M	5.0
J-013	68.21	26.79	5.00	1.5	1600/6 + 1400/38	M + R ²	5.4
J-014	67.49	26.51	6.00	1.5	1600/6 + 1400/38	M + R	5.6
J-015 ³	67.85	26.65	5.00	1.5	1600/6 + 1400/38	M + R	5.3
J-016 ⁴	66.76	26.23	6.00	1.5	1600/6 + 1400/38	M + R	5.6
J-005	67.30	26.49	6.21	1.5	1600/8 + 1200/11	M + R	5.6
J-006	66.62	23.13	10.25	1.7	1600/8 + 1200/11	M + AT ⁵	5.2
J-007	62.73	24.60	12.67	1.5	1600/8 + 1200/11	M + AT	3.5
J-008	62.15	21.55	16.30	1.7	1600/8 + 1200/11	M + AT	3.0
J-017	60.09	23.61	16.30	1.5	1600/12 + 1400/38	M + AT	3.2
J-018	64.65	19.05	16.30	2.0	1600/12 + 1400/38	M + AT	3.9
J-019	60.19	20.81	19.00	1.7	1600/12 + 1400/38	M + AT	2.5
J-020	57.96	20.04	22.00	1.7	1600/12 + 1400/38	M + AT	2.3
J-035	54.07	15.93	30.00	2.0	1100/4 + 1500/56	M + AT	2.0
J-036	47.32	12.68	40.00	2.2	1100/4 + 1500/56	M + AT + R	N.A. ⁶

1. Mullite(ss) as a major phase

2. rutile

3. 0.5 wt% MgO added

4. 1.01 wt% MgO added

5. aluminum titanate(ss)

6. not available

Table 9. Summary of TiO_2 -Mullite Compositions Synthesized by Sol-Gel Processing

Sample No.	Composition	A/S	Sintering ($^{\circ}\text{C}/\text{h}$)	Phase(s) present	CTE($^{\circ}\text{C} \times 10^{-6}$) R.T.-1000 $^{\circ}\text{C}$
J-082	$\text{Al}_6\text{Ti}_{0.1}\text{Si}_{1.9}\text{O}_{13}$	1.58	1500/72	M	5.0
J-083	$\text{Al}_6\text{Ti}_{0.2}\text{Si}_{1.2}\text{O}_{13}$	1.67	1500/72	M	5.1
J-084	$\text{Al}_6\text{Ti}_{0.3}\text{Si}_{1.7}\text{O}_{13}$	1.76	1500/72	M + AT(tr)	N.A.
J-0901	$\text{Al}_{5.6}\text{Ti}_{0.3}\square_{0.1}\text{Si}_2\text{O}_{13}$	1.40	1350/72	M + R(mi)	N.A.
J-0902	$\text{Al}_{5.6}\text{Ti}_{0.3}\square_{0.1}\text{Si}_2\text{O}_{13}$	1.40	1450/72	M + AT(tr)	N.A.
J-0903	$\text{Al}_{5.6}\text{Ti}_{0.3}\square_{0.1}\text{Si}_2\text{O}_{13}$	1.40	1500/72	M + AT(tr)	N.A.
J-0904	$\text{Al}_{5.6}\text{Ti}_{0.3}\square_{0.1}\text{Si}_2\text{O}_{13}$	1.40	1550/72	M + AT(tr)	4.8
J-0905	$\text{Al}_{5.6}\text{Ti}_{0.3}\square_{0.1}\text{Si}_2\text{O}_{13}$	1.40	1600/72	M + AT(tr) + R(tr)	N.A.
J-0906	$\text{Al}_{5.6}\text{Ti}_{0.3}\square_{0.1}\text{Si}_2\text{O}_{13}$	1.40	1650/20	M + R(tr)	N.A.
J-0907	$\text{Al}_{5.6}\text{Ti}_{0.3}\square_{0.1}\text{Si}_2\text{O}_{13}$	1.40	melted	M + R(tr)	N.A.
J-091	$\text{Al}_{5.73}\text{Ti}_{0.19}\square_{0.07}\text{Si}_2\text{O}_{13}$	1.44	1550/72	M	4.6
J-093	$\text{Al}_{5.76}\text{Ti}_{0.18}\square_{0.06}\text{Si}_2\text{O}_{13}$	1.44	1550/72	M	5.0
J-094	$\text{Al}_{5.68}\text{Ti}_{0.24}\square_{0.08}\text{Si}_2\text{O}_{13}$	1.42	1550/72	M + AT(tr)	5.0

M = mullite(ss)

AT = Al_2TiO_5 (aluminum titanate)

R = rutile

N.A. = not available

tr = trace

mi = minor amount

Figure 11. Thermal expansion of TiO₂-modified mullite solid solutions.

mechanical properties because of the anisotropic expansion of Al_2TiO_5 ($\alpha_a = \alpha_b = -2.6 \times 10^{-6}/^\circ\text{C}$ and $\alpha_c = 11.5 \times 10^{-6}/^\circ\text{C}$).

Several samples containing 5-6 wt% TiO_2 were prepared to determine whether a small amount of MgO could promote more extensive TiO_2 solubility. It was observed that this addition neither increased the solubility of TiO_2 in mullite nor affected the thermal expansion behavior of the TiO_2 -mullite solid solution.

AlPO_4 - BPO_4 -Mullite Solid Solutions

Since AlPO_4 and BPO_4 are isostructural with SiO_2 , their ionic radii are of the proper size, and a charge balanced substitution exists, a limited solubility of both compounds in mullite can be expected. Also, $\text{P}^{5+}\text{-O}^{2-}$ and $\text{B}^{3+}\text{-O}^{2-}$ bonds have higher bond strengths than $\text{Si}^{4+}\text{-O}^{2-}$ and $\text{Al}^{3+}\text{-O}^{2-}$ bonds which indicate the possibility of lowering the CTE of mullite. Table 10 summarizes the compositions prepared, preparation technique, and the phases produced after reaction. The preparation procedures were modified several ways in order to obtain solid solution by maintaining high temperature equilibrium. The procedures attempted included: 1) Mixing of AlPO_4 and BPO_4 with mullite followed by high temperature reaction, 2) Mixing of ingredients such as H_3BO_3 and $(\text{NH}_4)_2\text{HPO}_4$ followed by high temperature reaction, 3) Mixing of AlPO_4 and BPO_4 with mullite in a sealed Pt tube which after reaction was quenched in ice water, and 4) Sol-gel formation followed by high temperature reaction. Even in compositions containing less than 3 wt% AlPO_4 and BPO_4 , multiphase assemblages were still observed by XRD.

XYO_4 -Mullite Solid Solutions

Other half-breed derivatives (excluding AlPO_4 and BPO_4) were also added to mullite by solid-state reaction using synthesized arsenate and XYO_4 compounds plus the raw materials: Cr_2O_3 , $(\text{NH}_4)_2\text{HPO}_4$, H_3BO_3 , Ga_2O_3 , $\text{Al}(\text{OH})_3 \cdot n\text{H}_2\text{O}$, and $\text{SiO}_2 \cdot n\text{H}_2\text{O}$. Of the compositions listed in Table 11, only GaAsO_4 formed mullite solid solution. Other compositions showed the

Table 10. Summary of AlPO_4 - BPO_4 -Mullite Compositions

Sample No.	Composition (wt%)				A/S	Sintering ($^{\circ}\text{C}/\text{h}$)	Phase(s) present	CTE($^{\circ}\text{C}\times 10^{-6}$) R.T.-1000 $^{\circ}\text{C}$
J-022 ¹	66.77	26.23	7.00	--	1.5	1600/5+1500/72	M ⁵ + AP ⁶ (t) + C ⁷ (t) ⁹	5.3
J-023 ¹	63.18	24.82	12.00	--	1.5	1600/5+1500/72	M + AP(t) + C(t)	5.4
J-024 ¹	59.59	23.41	17.00	--	1.5	1600/5+1500/72	M + AP(t)	--
J-026 ¹	61.67	26.33	12.00	--	1.38	1600/5+1500/72	M + AP(t)	5.4
J-027 ¹	66.87	26.13	--	7.00	1.5	1550/18	M + ABP ⁸ (t) + C(t)	5.0
J-028 ¹	63.23	24.72	--	12.00	1.5	1550/18	M + ABP(t)	5.5
J-029 ²	64.70	25.30	2.78	7.22	1.5	1550/18	M + ABP(t) + C(t)	--
J-030 ²	64.70	25.30	5.36	4.64	1.5	1550/18	M + ABP(t) + C(t)	--
J-031 ²	64.70	25.30	7.76	2.24	1.5	1550/18	M + ABP(t) + C(t)	--
J-032 ³	68.31	26.69	5.00	--	1.5	1500/12+1600/18	M + AP(t) + C(t)	--
J-033 ³	68.31	26.69	--	5.00	1.5	1500/12+1600/18	M + ABP(t) + C(t)	--
J-034 ³	64.70	25.30	5.00	5.00	1.5	1500/12+1600/18	M + ABP(t) + C(t)	--
J-036 ²	59.56	28.08	--	12.36	1.25	1500/27	M + ABP(t)	5.8
J-057 ²	58.46	27.56	13.98	--	1.25	1500/27	M + AP(t)	5.6
J-067 ⁴	68.40	26.87	--	4.73	1.5	1500/27	M + ABP(t)	--
J-068 ⁴	67.91	26.68	5.41	--	1.5	1500/12	M + AP(t)	--
J-075 ²	71.76	25.37	2.86	--	1.67	1500/216	M + AP(t) + C(t)	--
J-076 ²	72.04	25.47	--	2.49	1.67	1500/216	M + ABP(t) + C(t)	--

1. Synthesized AlPO_4 and BPO_4 were used as raw materials.

2. $(\text{NH}_4)_2\text{HPO}_4$ and H_3BO_3 were used as the sources of P_2O_5 and B_2O_3 .

3. Sample was sintered in a sealed Pt-tube and quenched in ice water. Powders were reagent grade SiO_2 , Al_2O_3 , AlPO_4 , and BPO_4 .

4. Samples were prepared by sol-gel processing.

5. M = mullite(ss)

6. AP = AlPO_4

7. C = corundum

8. ABP = $(\text{Al,B})\text{PO}_4$

9. t = trace amount

Table 11. Summary of XYO_4 -Mullite Compositions

Sample No.	Composition (wt%)			A/S	Sintering ($^{\circ}\text{C}/\text{h}$)	Phase(s) Present	CTE($^{\circ}\text{C} \times 10^{-6}$) R.T.-1000 $^{\circ}\text{C}$
	Al_2O_3	SiO_2	XYO_4				
J-052	68.20	26.80	5.00GaPO ₄	1.5	1500/24	M ² + C ³ (t) ⁴	5.8
J-053	68.20	26.80	5.00CrPO ₄	1.5	1550/24	M + C(t)	5.6
J-058	62.63	27.34	10.03CrPO ₄	1.35	1550/27	M + (Al,Cr)PO ₄	5.6
J-059	61.88	27.01	11.11GaPO ₄	1.35	1550/27	M + (Al,Ga)PO ₄	5.0
J-060	65.54	27.59	6.87BaSO ₄	1.4	1550/42	M + g ⁵ (t)	5.3
J-061	65.06	27.38	7.56AlAsO ₄	1.4	1550/42	M + g(t)	5.2
J-062	63.81	26.86	9.33GaAsO ₄	1.4	1550/42	M + g(t)	5.0
J-063	60.10	26.23	13.66GaAsO ₄	1.35	1550/30	M	5.1
J-077 ¹	71.05	25.12	3.83GaPO ₄	1.67	1500/216	M + (Al,Ga)PO ₄ (t) + C(t)	--
J-078 ¹	71.35	25.23	3.43CrPO ₄	1.67	1500/216	M + (Al,Cr)PO ₄ (t) + C(t)	--
J-079	71.30	25.21	3.49BaSO ₄	1.67	1500/216	M + C(t)	--
J-080	71.03	25.11	3.85AlAsO ₄	1.67	1500/216	M + C(t)	--
J-081	70.33	24.87	4.80GaAsO ₄	1.67	1500/216	M + C(t)	--

1. Prepared by solid-state reaction with Ga_2O_3 , Cr_2O_3 , and $(\text{NH}_4)_2\text{HPO}_4$ as raw materials

2. M = mullite(ss)

3. C = corundum

4. t = trace amount

5. g = glassy phase

formation of two or more phases. A small amount of liquid phase formation was observed in preparations containing BaAsO_4 , AlAsO_4 , and GaAsO_4 .

Single Oxide-Mullite Solid Solutions

Oxides of the form A_xO_y were reacted with mullite in an effort to form a solid solution. The compositions, heat treatments, phase analyses, and CTE values are listed in Table 12. The results are summarized for each oxide below.

(1) P_2O_5 did not show significant solubility in mullite, even though P^{5+} ions are readily incorporated into many other silicates in the $[\text{SiO}_4]$ positions. This phenomenon may be explained by the formation of very stable AlPO_4 consuming most of the P_2O_5 before it diffuses into the mullite structure.

(2) Ga_2O_3 showed solubility in mullite with the stoichiometry of: $\text{Al}_{6-x}\text{Ga}_x\text{Si}_2\text{O}_{13}$ where x varies from 0 to 1.8. The solid solutions were prepared by both solid-state reaction and sol-gel decomposition techniques. Solid solution compositions did not yield CTE values significantly different from mullite.

(3) GeO_2 was found to form a complete solid solution series between $\text{Al}_6\text{Si}_2\text{O}_{13}$ - $\text{Al}_6\text{Ge}_2\text{O}_{13}$ with Ge^{4+} substituting for Si^{4+} in the tetrahedral sites. Based on the stoichiometry $\text{Al}_6(\text{Si}_{2-x}\text{Ge}_x)\text{O}_{13}$, specimens with x values up to 2 were investigated. The CTE did not change significantly with the addition of GeO_2 .

(4) B_2O_3 additions showed significant solid solubility but no significant change in CTE was observed. Also, liquid phase formation was frequently observed even with low heating rates.

(5) Cr_2O_3 additions for maximum solubility in mullite are in the form of $\text{Al}_{5.48}\text{Cr}_{0.52}\text{Si}_2\text{O}_{13}$. Since the CTE values show a slight decrease in comparison with stoichiometric mullite, it is suggested that this solid solution composition be studied further.

(6) WO_3 -modified mullite with stoichiometry $\text{Al}_{6-2x}\text{W}_x\text{Si}_2\text{O}_{13}$ was prepared. WO_3 was not soluble in mullite probably due to the large difference in the valence states of Al and W.

Table 12. Summary of Single Oxide-Mullite Compositions

Sample No.	Composition	A/S	Sintering (°C/h)	Phase(s) Present	CTE(°C×10 ⁶) R.T.-1000°C
J-039	Al ₆ Si _{1.175} P _{0.1} □ _{0.025} O ₁₃	1.60	1550/24	M ³ + AP ⁴ (l) ⁷	--
J-040	Al ₆ Si _{1.75} P _{0.2} □ _{0.05} O ₁₃	1.71	1550/24	M + AP(l) + C ⁵ (l)	--
J-069 ¹	Al _{5.91} Si _{1.17} P _{0.152} □ _{0.0324} O ₁₃	1.58	1500/100	M + AP(l)	--
J-037	Al _{5.4} Ga _{0.6} Si ₂ O ₁₃	1.35	1500/56	M	4.9
J-041	Al ₅ Ga Si ₂ O ₁₃	1.25	1500/56	M + G ⁶ (l)	4.8
J-042	Al _{4.6} Ga _{1.4} Si ₂ O ₁₃	1.15	1500/56	M + G(l)	4.8
J-048	Al ₆ Gc ₂ O ₁₃	--	1450/48	Gc-M	5.2
J-038	Al _{5.4} Ga _{0.6} Si _{1.5} Gc _{0.5} O ₁₃	1.8	1500/56	M + C(l)	5.2
J-044	Al ₅ GaSi _{1.5} Gc _{0.5} O ₁₃	1.67	1500/56	M + C(l)	5.1
J-045	Al _{5.1} Ga _{0.6} Ti _{0.2} □ _{0.07} Si ₂ O ₁₃	1.28	1550/24	M + G(l)	4.9
J-047	Al _{5.4} Ga _{0.3} Ti _{0.2} □ _{0.07} Si ₂ O ₁₃	1.35	1550/24	M	5.0
J-046	Al _{5.1} Ga _{0.6} Ti _{0.2} □ _{0.07} Si _{1.75} Gc _{0.25} O ₁₃	1.46	1550/24	M	5.1
J-054	Al _{5.2} B _{0.1} Si ₂ O ₁₃	1.3	1550/30	M	5.0
J-055	Al _{4.1} B _{1.2} Si ₂ O ₁₃	1.2	1550/30	M	5.1
J-072 ¹	Al _{5.2} B _{0.1} Si ₂ O ₁₃	1.3	1550/100	M	5.2
J-049 ²	Al _{5.42} Cr _{0.52} Si ₂ O ₁₃	1.37	1550/30 + 1600/24	M	4.7
J-050	Al _{5.1} W _{0.1} □ _{0.1} Si ₂ O ₁₃	1.45	1550/24	M + W ⁸ (l)	5.4
J-051	Al _{5.6} W _{0.2} □ _{0.2} Si ₂ O ₁₃	1.4	1550/24	M + W(l)	5.5

1. Synthesized by sol-gel processing

2. Amount of Cr₂O₃ used corresponds to its solid solubility in mullite at 1600°C

3. M = mullite(ss)

4. AP = AlPO₄

5. C = corundum

6. G = α-Ga₂O₃

7. l = trace amount

8. W = WO₃

Summary

1. Of the substitutions attempted in mullite, only TiO_2 reduced the thermal expansion coefficient significantly.
2. The addition of 3 wt% TiO_2 in mullite reduced the thermal expansion coefficient by about 10%.
3. Substitution of half-breed derivatives such as AlPO_4 , BPO_4 , etc. in mullite is limited and equilibrium is difficult to achieve. Single oxides investigated, except for GeO_2 and Ga_2O_3 , have low solubilities in mullite.
4. Sol-gel processing appeared to decrease the time required for mullite formation at high temperatures, but produced the same solubility and phase assemblage as solid-state reaction processing.

ZIRCON (NZP) SYSTEM

A thorough investigation of the thermal expansion behavior of NZP compounds via extensive ionic substitution has resulted in new compositions which exhibit nearly zero expansion and excellent thermal shock resistance. Based on the thermal expansion data, a screening test was first conducted on 25 different NZP compounds synthesized with Na^+ substitutions by cations with 1+ to 5+ valences. The compounds showing low thermal expansion were then subjected to tests including axial thermal expansion, thermal shock resistance, modulus of rupture (MOR), sinterability, and structural stability to further assist in selecting the optimum compositions for heat engine applications.

Low Thermal Expansion Compositions

Elements selected to replace Na in the NZP structure are summarized in Table 13; the ionic radii are based on a coordination number of 6. The compositions which showed low aggregate thermal expansion and axial thermal expansion are presented in Table 14. The $(\text{Rb}_{0.5}, \text{Cs}_{0.5})\text{Zr}_2(\text{PO}_4)_3$ composition has a CTE value close to zero ($-0.3 \times 10^{-7}/^\circ\text{C}$), while $\text{RbZr}_2(\text{PO}_4)_3$, $\text{CsZr}_2(\text{PO}_4)_3$, and $(\text{Ca}_{0.5}, \text{Mg}_{0.5})\text{Zr}_4(\text{PO}_4)_3$ show thermal expansion behavior comparable to that of fused silica with CTE values of $2 \times 10^{-7}/^\circ\text{C}$, $5 \times 10^{-7}/^\circ\text{C}$, and $-5 \times 10^{-7}/^\circ\text{C}$,

Table 13. Ionic Radii of Elements Selected to Modify the NZP Structure

Elements Ionic with +1 Radii valence (Å)	Elements Ionic with +2 Radii valence (Å)	Elements Ionic with +3 Radii valence (Å)	Elements Ionic with +4 Radii valence (Å)	Elements Ionic with +5 Radii valence (Å)
Li 0.68	Mg 0.74	Y 0.97	Ti 0.64	V 0.4
Na 0.98	Ca 1.04	La 1.04	Zr 0.82	Nb 0.66
K 1.33	Sr 1.20	Al 0.57	Hf 0.82	Ta 0.66
Rb 1.49	Ba 1.20	Cr 0.64	Si 0.39	
Cs 1.65	Mn 0.91		Ce 0.88	
	Ni 0.74			
	Cu 0.80			
	Zn 0.83			

Table 14. Axial and Linear CTE Values for Selected Systems with Low CTE

System	Axial CTE		Calculated		$ a_c/a_a $
	$(\times 10^{-7}/^{\circ}\text{C})$		a_1	a_1	
	a_a	a_c	$(\times 10^{-7}/^{\circ}\text{C})$	$(\times 10^{-7}/^{\circ}\text{C})$	
$\text{RbZr}_2(\text{PO}_4)_3$	-12	30	2	2	2.50
$\text{CsZr}_2(\text{PO}_4)_3$	-9	23	2	5	2.56
$\text{MgZr}_4(\text{PO}_4)_6$	-22	58	5	16	2.64
$\text{CaZr}_4(\text{PO}_4)_6$	-38	79	1	-18	2.08
$\text{BaZr}_4(\text{PO}_4)_6$	-67	279	45	15	4.16
$\text{MnZr}_4(\text{PO}_4)_6$	-51	112	3	7	2.20
$\text{NiZr}_4(\text{PO}_4)_6$	-70	172	10	10	2.46
$\text{YZr}_6(\text{PO}_4)_9$	-27	62	3	14	2.30
$\text{TiZr}_8(\text{PO}_4)_{12}$	-30	34	-9	20	1.13
$\text{CoZr}_8(\text{PO}_4)_{12}$	-35	57	-4	11	1.63
$\text{NbZr}(\text{PO}_4)_3$	24/-25	-61/79	-4/10	4	2.54/3.16
$\text{TaZr}(\text{PO}_4)_3$	38/-35	-35/78	13/1	11	0.92/2.23
$(\text{Rb}_{0.5}, \text{Cs}_{0.5})\text{Zr}_2(\text{PO}_4)_3$	-11	21	-0.3	-0.3	1.91
$(\text{Ca}_{0.5}, \text{Mg}_{0.5})\text{Zr}_4(\text{PO}_4)_6$	-39/-14	66/47	-4/6	-5	1.69/3.36
$(\text{Ca}_{0.375}, \text{Mg}_{0.125})\text{Zr}_2(\text{PO}_4)_3$	-47/-18	81/67	-4/10	-10	1.72/3.72

respectively. The axial thermal expansion behavior of the synthesized compounds showed similarity to that of the Na-NZP, that is, *a*-axis contracts and *c*-axis expands. The degree of thermal expansion anisotropy was greatly reduced possibly due to the substitutions of larger ions, especially for the $(\text{Rb}_{0.5}, \text{Cs}_{0.5})\text{Zr}_2(\text{PO}_4)_3$ and $(\text{Ca}_{0.5}, \text{Mg}_{0.5})\text{Zr}_4(\text{PO}_4)_6$ compositions as shown in Figures 12 to 16. The optimum composition should possess not only low aggregate thermal expansion but also minimum anisotropy in axial thermal expansion in order to attain high thermal shock resistance and mechanical strength. The discrepancy between the measured and calculated α in certain compositions possibly reflects the formation of microcracks resulting from the highly anisotropic axial expansion. Therefore, among all the low expansion NZP compounds shown in Table 14, the compositions derived from the substitutions of Rb, Cs, and the combination of Ca and Mg appear to be most promising and were further characterized.

Phase Relations

Crystal chemical studies based on the $(\text{Rb}_{1-x}, \text{Cs}_x)\text{Zr}_2(\text{PO}_4)_3$ compositions indicate that a complete solid solution exists between the Rb and Cs end members as shown in Figure 17. However, only limited solid solution was found for the $(\text{Ca}_{1-x}, \text{Mg}_x)\text{Zr}_4(\text{PO}_4)_6$ system as shown in Figure 18. It is likely that, like the Li^+ ion, the Mg^{2+} is too small for the Na^+ site and therefore decreases the stability of the crystal structure. Due to the volatile nature of P^{5+} , the heat treatment adopted in synthesis studies consists of three stages: calcining between 150°C and 550°C , forming the intermediate phase (ZrP_2O_7) at 1000°C , and forming the NZP phase between 1200°C to 1300°C .

Thermal Shock Resistance

Thermal shock resistance of the sintered bars was measured using the water quench method which involves the maximum quench temperature difference (ΔT_{max}) without observable cracking, and the number of repeated quenches from 1200°C . As shown in Table 15, the maximum quench temperature difference was 1475°C for the compound $(\text{Ca}_{0.5}, \text{Mg}_{0.5})\text{Zr}_4(\text{PO}_4)_6$:

Figure 12. Axial thermal expansion behavior of RbZr₂(PO₄)₃.

Figure 13. Axial thermal expansion behavior of $\text{CsZr}_2(\text{PO}_4)_3$.

Figure 14. Axial thermal expansion behavior of $(\text{Rb}_{0.5}\text{Cs}_{0.5})\text{Zr}_2(\text{PO}_4)_3$.

Figure 15. Axial thermal expansion behavior of $\text{CaZr}_4(\text{PO}_4)_6$.

Figure 16. Axial thermal expansion behavior of $(\text{Ca}_{0.5}\text{Mg}_{0.5})\text{Zr}_4(\text{PO}_4)_6$.

Figure 17. Lattice parameters for the $(\text{Rb}_x\text{Cs}_{1-x})\text{Zr}_2(\text{PO}_4)_3$ compositions.

Figure 18. Lattice parameters for the $(\text{Ca}_x, \text{Mg}_{1-x})\text{Zr}_4(\text{PO}_4)_6$ compositions.

Table 15. Thermal Shock Resistance of $(\text{Ca}_{0.5}\text{Mg}_{0.5})\text{Zr}_4(\text{PO}_4)_6$ and $(\text{Rb}_{0.5}\text{Cs}_{0.5})\text{Zr}_2(\text{PO}_4)_3$

Compound	Maximum Quench $\Delta T_m (^{\circ}\text{C})$	Allowable Repeated Quenches with $\Delta T = 1200^{\circ}\text{C}$
$(\text{Ca}_{0.5}\text{Mg}_{0.5})\text{Zr}_4(\text{PO}_4)_6$	1475	5
$(\text{Rb}_{0.5}\text{Cs}_{0.5})\text{Zr}_2(\text{PO}_4)_3$	>1675*	20**

* No cracking was observed up to the maximum temperature difference of 1625°C .

** No cracking was observed after 20 repeated quenches.

Table 16. MOR Data for $(\text{Ca}_{0.5}\text{Mg}_{0.5})\text{Zr}_4(\text{PO}_4)_6$ and $(\text{Rb}_{0.5}\text{Cs}_{0.5})\text{Zr}_2(\text{PO}_4)_3$

$(\text{Ca}_{0.5}\text{Mg}_{0.5})\text{Zr}_4(\text{PO}_4)_6$			$(\text{Rb}_{0.5}\text{Cs}_{0.5})\text{Zr}_2(\text{PO}_4)_3$		
Sample	3-point (MPa)	4-point (MPa)	Sample	3-point (MPa)	4-point (MPa)
1	26.44	18.70	1	50.52	46.67
2	20.12	23.46	2	52.25	46.59
3	20.46	20.67	3	54.57	53.71
4	24.03	21.26	4	50.06	47.57
5	24.59	23.33	5	56.16	51.18
Average	23.13	21.48	Average	52.71	49.14

however, the compound $(\text{Rb}_{0.5}, \text{Cs}_{0.5})\text{Zr}_2(\text{PO}_4)_3$ resisted fracture up to 1625°C . The sample $(\text{Ca}_{0.5}, \text{Mg}_{0.5})\text{Zr}_4(\text{PO}_4)_6$ cracked after 6 repeated quenches, while the specimen $(\text{Rb}_{0.5}, \text{Cs}_{0.5})\text{Zr}_2(\text{PO}_4)_3$ withstood 20 thermal cycles.

Modulus of Rupture

MOR Data were obtained from 3-point and 4-point bending tests, and their average values are summarized in Table 16. Average MOR values of $(\text{Rb}_{0.5}, \text{Cs}_{0.5})\text{Zr}_2(\text{PO}_4)_3$ (49.14 and 52.71 MPa from 4-point and 3-point, respectively) were over twice those of $(\text{Ca}_{0.5}, \text{Mg}_{0.5})\text{Zr}_4(\text{PO}_4)_6$ (21.48 and 23.13 MPa from 4-point and 3-point bending test, respectively). It is expected that the MOR values can be considerably increased by hot isostatic pressing and control of grain size.

Bulk Density and Porosity

The percent theoretical density (TD) for both compounds exceeded 94% as shown in Table 17. Open porosities were measured as 4.5% and 3.4% for $(\text{Ca}_{0.5}, \text{Mg}_{0.5})\text{Zr}_4(\text{PO}_4)_6$ and $(\text{Rb}_{0.5}, \text{Cs}_{0.5})\text{Zr}_2(\text{PO}_4)_3$, respectively. Sample shrinkage was larger in $(\text{Rb}_{0.5}, \text{Cs}_{0.5})\text{Zr}_2(\text{PO}_4)_3$ (12.5%) than in $(\text{Ca}_{0.5}, \text{Mg}_{0.5})\text{Zr}_4(\text{PO}_4)_6$ (10.6%). Meanwhile, more water was absorbed in $(\text{Ca}_{0.5}, \text{Mg}_{0.5})\text{Zr}_4(\text{PO}_4)_6$ (1.44%) than in $(\text{Rb}_{0.5}, \text{Cs}_{0.5})\text{Zr}_2(\text{PO}_4)_3$ (1.03%).

Table 17. Structural Attributes of $(\text{Ca}_{0.5}, \text{Mg}_{0.5})\text{Zr}_4(\text{PO}_4)_6$
and $(\text{Rb}_{0.5}, \text{Cs}_{0.5})\text{Zr}_2(\text{PO}_4)_3$

<u>Compound</u>	<u>% Shrinkage</u>	<u>Bulk Density (g/cm³)</u>	<u>%TD</u>	<u>% Open Porosity</u>	<u>%Water Absorption</u>
$(\text{Ca}_{0.5}, \text{Mg}_{0.5})\text{Zr}_4(\text{PO}_4)_6$	10.6	3.101	94.1	4.5	1.41
$(\text{Rb}_{0.5}, \text{Cs}_{0.5})\text{Zr}_2(\text{PO}_4)_3$	12.5	3.202	95.9	3.4	1.03

Structural Stability

High temperature phase stability of the two systems $(\text{Rb}_{1-x}\text{Cs}_x)\text{Zr}_2(\text{PO}_4)_3$ and $(\text{Ca}_{1-x}\text{Mg}_x)\text{Zr}_4(\text{PO}_4)_6$ was determined by heating samples at elevated temperatures for different lengths of time followed by XRD examination for signs of phase decomposition. For the $(\text{Rb}_{1-x}\text{Cs}_x)\text{Zr}_2(\text{PO}_4)_3$ system, all samples showed signs of decomposition after heat treatment at 1300°C for 114 hours. The $\text{RbZr}_2(\text{PO}_4)_3$ end of the series showed higher stability than the $\text{CsZr}_2(\text{PO}_4)_3$ end. Another compositional series was heated at 1200°C for 72 hours and then heated at 1250°C for 94 hours. No significant signs of decomposition were detected. The results suggest that the upper temperature limit of stability for the Rb-Cs system lies between 1250°C and 1300°C . For the system $(\text{Ca}_{1-x}\text{Mg}_x)\text{Zr}_4(\text{PO}_4)_6$, samples were heated from 1220°C to 1450°C for 36 to 84 hours. No signs of decomposition were observed for compositions at the $\text{CaZr}_4(\text{PO}_4)_6$ end, while compositions high in Mg decomposed to $\text{Zr}_2\text{P}_2\text{O}_9$ at temperatures higher than 1350°C .

Summary

1. Among all the synthesized NZP compounds, the Rb-Cs and Ca-Mg substituted compositions exhibited nearly zero aggregate thermal expansion and low thermal expansion anisotropy.
2. $(\text{Rb}_{0.5}\text{Cs}_{0.5})\text{Zr}_2(\text{PO}_4)_3$ exhibited better thermal shock resistance than $(\text{Ca}_{0.5}\text{Mg}_{0.5})\text{Zr}_4(\text{PO}_4)_6$.
3. The MOR value of $(\text{Rb}_{0.5}\text{Cs}_{0.5})\text{Zr}_2(\text{PO}_4)_3$ was more than twice that of $(\text{Ca}_{0.5}\text{Mg}_{0.5})\text{Zr}_4(\text{PO}_4)_6$.
4. The sinterability was approximately the same for $(\text{Rb}_{0.5}\text{Cs}_{0.5})\text{Zr}_2(\text{PO}_4)_3$ and $(\text{Ca}_{0.5}\text{Mg}_{0.5})\text{Zr}_4(\text{PO}_4)_6$.
5. $(\text{Ca}_{0.5}\text{Mg}_{0.5})\text{Zr}_4(\text{PO}_4)_6$ was more stable than $(\text{Rb}_{0.5}\text{Cs}_{0.5})\text{Zr}_2(\text{PO}_4)_3$ at high temperature.

CONCLUSIONS AND RECOMMENDATIONS

Since the inception of the AGT program in 1979 until the present, few (if any) new ceramic compositions have been identified that even suggest possible applications in heat engines. Through a subcontract with Oak Ridge National Laboratory's Ceramic Technology for Advanced Heat Engines Project, Virginia Tech has been attempting to develop new ceramic compositions with near zero thermal expansion for use to at least 1200°C. As a result of this work, several new ceramic formulations have been identified which show considerable early promise for heat engine applications. The results of screening and property characterization of the four ceramic systems may be summarized as follows:

1. AlPO_4 - β -eucryptite - The solid solubility limit of AlPO_4 in β -eucryptite was found to be 54 mole % AlPO_4 . A small amount of nonstoichiometric SiO_2 substituted in β -eucryptite decreases the melting temperature and reduces the negative bulk thermal expansion coefficient. Up to 20 mole % Li^+ can be substituted for Mg^{2+} in β -eucryptite and decreases the negative thermal expansion and expansion anisotropy. Two compositions with improved thermal expansion properties were identified, $\text{Li}_{0.5}\text{AlP}_{0.5}\text{Si}_{0.465}\text{O}_{3.93}$ and $\text{Li}_{0.41}\text{Mg}_{0.35}\text{AlP}_{0.52}\text{Si}_{0.48}\text{O}_4$. These compositions have thermal expansion coefficients of -0.76×10^{-7} and $-2.3 \times 10^{-7}/^\circ\text{C}$, respectively, and thermal conductivities of about 2.22 W/m·K at 100°C.

2. β -Cristobalite - Solid solutions of BPO_4 , AlPO_4 , and TiO_2 in β -cristobalite were unsuccessful in reducing the $\alpha \rightarrow \beta$ phase transition temperature to below room temperature. The lowest transformation temperature observed was 167°C when AlPO_4 and TiO_2 were simultaneously added to SiO_2 . Both β -cristobalite and β -quartz were successfully stabilized to room temperature by sol-gel preparation when $\text{CaO}/\text{Al}_2\text{O}_3$ and $\text{CuO}/\text{Al}_2\text{O}_3$ substitutions were present. The stabilized β -cristobalite phases were not low expanding. Typical bulk linear expansion coefficients were $80 \times 10^{-7}/^\circ\text{C}$.

3. Mullite - Solid-state reaction and sol-gel techniques were used to form chemically-modified mullite solid solutions in an effort to lower the thermal expansion. TiO_2 , B_2O_3 , CrPO_4 , P_2O_5 , Ga_2O_3 , Cr_2O_3 , and WO_3 and the half-breed SiO_2 compounds AlPO_4 , BPO_4 , GaPO_4 , BAsO_4 , AlAsO_4 , GaAsO_4 , and

GeO_2 were studied. Apart from TiO_2 , none of the substitutions significantly changed the thermal expansion properties. The solubility of 3 wt% TiO_2 in mullite reduced the coefficient of thermal expansion by about 10%.

4. Zircon - $\text{NaZr}_2(\text{PO}_4)_3$ (NZP) is a zircon derivative structure which is capable of accepting a wide range of oxides into solid solution. A large number of NZP compositions were prepared and several showed low thermal expansion behavior. Two solid solutions in particular, $(\text{Ca},\text{Mg})\text{Zr}_4(\text{PO}_4)_6$ and $(\text{Rb},\text{Cs})\text{Zr}_2(\text{PO}_4)_3$, were found to have nearly zero linear thermal expansion up to 1200°C . In addition, these compositions were found to have thermal conductivities of approximately $0.6 \text{ W/m}\cdot\text{K}$. The NZP structures clearly represent a new class of high melting, thermal shock-resistant ceramics.

The most promising new ceramics identified are a result of composition modifications of the $\text{NaZr}_2(\text{PO}_4)_3$ (NZP) structure. A wide range of chemical substitutions is possible in this structure and considerable property modification is also possible. As a result of a systematic screening of the thermal expansion characteristics of chemically modified NZP, many low expanding formulations were identified and two are of particular interest: $(\text{Ca}_{0.5},\text{Mg}_{0.5})\text{Zr}_4(\text{PO}_4)_6$ and $(\text{Rb}_{0.5},\text{Cs}_{0.5})\text{Zr}_2(\text{PO}_4)_3$. These compositions are stable to 1500°C and above, possess nearly zero aggregate linear thermal expansion, have low expansion anisotropy, and have demonstrated outstanding thermal shock resistance. In addition, it is expected that they will also have low thermal conductivities, comparable to other zirconium containing compounds.

A second class of new formulations that show promise includes the chemically modified β -eucryptite- AlPO_4 compositions. It has been known for many years that these solid solutions exhibit very low expansion; however, the present work has demonstrated that small compositional variations can greatly reduce the thermal expansion anisotropy. This reduces the microcracking upon thermal cycling and improves the thermal shock and thermal fatigue resistance. Modified β -eucryptite solid solutions fuse at about 1300°C and cannot be expected to have the lower thermal conductiveness of the NZP compositions; however, because lithia-alumina-silicate components are presently used in prototype heat engines, an improvement in thermal shock characteristics would be a significant advancement.

Up to this time, this research has concentrated on screening compositions in several crystal structure groups to identify high melting phases with low thermal expansion. Property characterization, other than thermal expansion and phase identification, has been on "as-prepared" samples. Sample porosities, generally in excess of 10%, preclude the collection of any significant mechanical properties data. It is felt that the prime objective of the continuation of this research should be to develop these materials through processing, composition optimization, characterization and parts fabrication to the point where they are attractive for testing in actual heat engines.

PART II. DEVELOPMENT OF ZIRCON AND MODIFIED β -EUCRYPTITE.

INTRODUCTION

The need for fabricable low expansion ceramics in advanced heat engines has been established by the Ceramic Technology Program of the Department of Energy. Ceramic systems suitable for use in advanced engines must not only exhibit low thermal expansion but also relatively high mechanical strength, thermal shock resistance, corrosion resistance, and stability to at least 1200°C. In the first phase of this study, the investigators examined candidate ceramics in the aluminum phosphate, silica, mullite and zircon systems. Of these ceramics, the aluminum phosphate β -eucryptite and zircon systems were selected for further study (Part I of this report) with the aim of optimizing the chemistry, properties, and processing of selected low thermal expansion compositions. The major objectives of this study were to demonstrate fabricability, determine thermo-mechanical properties, and to promote commercialization of these ceramics.

ZIRCON (NZP) SYSTEM

Since the first determination of the crystal structure of sodium zirconium phosphate $\text{NaZr}_2(\text{PO}_4)_3$ (NZP) by Hagman and Kierkegaard¹ in 1968, much attention has been drawn to this ceramic family. The research emphasis in the

1970s was placed on developing fast ionic conductors, known as NASICON ($\text{Na}_3\text{Zr}_2\text{SiP}_2\text{O}_{12}$), in this family.

In 1979, Boilot et. al.² reported a low negative thermal expansion associated with the compound. Since then, researchers have worked on developing new compounds with low thermal expansions from the NZP family.³⁻⁶ In particular, two compositions, $(\text{Rb}_{1-x}\text{Cs}_x)\text{Zr}_2(\text{PO}_4)_3$ (RCZP) and $(\text{Ca}_{1-x}\text{Mg}_x)\text{Zr}_4(\text{PO}_4)_6$ (CMZP), were evaluated. The study of RCZP was discontinued after it was discovered that RCZP decomposed at 1000°C as described in the following report. The study of CMZP was expanded to include lightweight CMZP, SiC whisker and chopped fiber reinforced CMZP, and in-situ NZP reinforced CMZP.

Synthesis of NZP

To produce NZP materials having higher density, techniques to synthesize more reactive powders were investigated. Sol-gel processes were developed to make CMZP and RCZP. Utilizing the sol-gel method, powders having a particle size as small as 20 nm were produced yielding compacts with densities 94% theoretical after cold pressing and sintering. Two different sol-gel processes were used to make CMZP with the starting materials $\text{Ca}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$, $\text{ZrO}(\text{NO}_3)_2$, and $\text{NH}_4\text{H}_2\text{PO}_4$.

In Process 1, zirconium solution is first added to a selected stoichiometric mix of calcium and magnesium nitrate, then phosphate solution is added drop by drop. The solutions are stirred constantly throughout the entire process. NH_4OH is then added to adjust the pH to 8-9 forming a homogeneous gel. The gel is stir dried at 40-60°C, oven dried at 110°C, and heat treated to form an ultra-fine CMZP powder. In Process 2, the three nitrates are mixed. Then while constantly stirring the mixture, the hydroxide and phosphate are added alternately drop by drop, maintaining a pH of 7. This solution is heated at 60-80°C, forming a dry-gel, then heat treated at 600-700 °C, forming a fine CMZP powder. The technique used to make RCZP is similar to Process 1.

Thermal Expansion of CMZP

The axial thermal expansion characteristics of $(\text{Ca}_{1-x}\text{Mg}_x)\text{Zr}_4(\text{PO}_4)_6$ (CMZP) ceramics were investigated to determine the degree of anisotropic thermal expansion. The anisotropic expansion of CMZP synthesized by solid state reaction methods was examined by X-ray diffraction (XRD) from room temperature to 750°C at the ORNL HTML. The resulting data are presented in Figure 19 along with axial expansion of other CMZP compositions where $x = 0.0, 0.2, \text{ and } 0.4$.

As shown, the anisotropic expansions of the *a* and *c* lattice parameters decrease with increasing Mg concentration. For the composition where $x = 0.4$, the thermal expansion anisotropy is significantly reduced. Expansion along the *a* axis for this composition is almost zero and the *c*-axis expansion is less than that of compositions containing less Mg. A reduction in the anisotropic expansion should contribute to a reduction of temperature-produced stress and possible microcrack formation, and hence, improve the thermal shock resistance of the material.

The overall bulk thermal expansion coefficients for the above mentioned compositions computed from the lattice parameters are as follows:

<u>MgZr₄(PO₄)₆ Content</u> <u>(mole %)</u>	<u>Bulk CTE</u> <u>($\times 10^{-7}/^\circ\text{C}$)</u>
0.0	-4.40
0.2	-0.74
0.3	-4.46
0.4	+4.76

Thermal Conductivity of CMZP

Thermal conductivities of the compositions $(\text{Ca}_{1-x}\text{Mg}_x)\text{Zr}_4(\text{PO}_4)_6$ where $x = 0.0, 0.2, 0.3, \text{ and } 0.5$ were obtained using a laser flash thermal diffusivity apparatus and a differential scanning calorimeter (DSC) at the ORNL HTML. The thermal conductivity values were calculated by the product of the thermal

Figure 19. Comparison of axial expansions for $(\text{Ca}_{1-x}\text{Mg}_x)\text{Zr}_4(\text{PO}_4)_6$ where $x = 0.0, 0.2$, and 0.4

diffusivity, specific heat, and bulk density of each sample. Acceptable values of thermal diffusivity at temperatures below 600°C were difficult to obtain, likely owing to the very low thermal diffusivity of the samples and resultant nonlinear heat flow. Densities of the CMZP ceramics synthesized by sol-gel process 1 ranged between 80% and 90% of theoretical.

Multiple DSC runs were made to determine the heat capacity of compositions of CMZP where $x = 0.0, 0.1, 0.2, 0.3, 0.4$, and 0.5 . Samples were evaluated relative to an empty Pt pan and the system was calibrated with a sapphire standard because the variation in specific heat values between each CMZP composition was not significant, the combined mean values of specific heat from all compositions are shown in Figure 20. It is believed that the specific heat values presented are representative of the range of compositions being studied.

Thermal conductivities of the CMZP compositions as a function of temperature are shown in Figure 21. It should be noted that these values are exceptionally low, and that thermal conductivity appears to decrease with increasing Mg content. Acceptable values of thermal diffusivity at temperatures below 600°C were difficult to obtain, likely owing to the very low thermal diffusivity of the samples and the resultant nonlinear heat flow.

Also shown in Figure 21 are the corresponding thermal conductivities of a partially stabilized (Y_2O_3) zirconia,³ a leading thermal barrier material for combustion and turbine engine applications. It is apparent that compared to the zirconia material, CMZP displays substantially lower thermal conductivities at each respective temperature.

Stability of CMZP

Thermal stabilities of the CMZP materials were determined using weight loss analyses. Powder samples of compositions where $x = 0.0, 0.2, 0.3$, and 0.4 were heated in platinum crucibles in air at 1200°C for 120 h. Weight losses were minimal in all specimens (less than 1%), and may be due to a reaction with the platinum crucibles.

Figure 20. Specific heat $(\text{Ca}_{1-x}\text{Mg}_x)\text{Zr}_4(\text{PO}_4)_6$ as a function of temperature

Figure 21. Thermal conductivities of CMZP compositions and stabilized zirconia

Effect of Sintering Conditions on CMZP

The effects of sintering temperature and time on the thermal expansion and microstructure of $(\text{Ca}_{0.6}\text{Mg}_{0.4})\text{Zr}_4(\text{PO}_4)_6$ (C6M4ZP) prepared using a solid-state reaction method were investigated. Bars containing 1 wt% ZnO (sintering aid) were pressed, and then sintered at temperatures of 1150°C to 1300°C. Densities greater than 95% of theoretical were achieved when the sintering temperature was higher than 1150°C. As shown in Figure 22, with an increase in sintering temperature from 1100°C to 1300°C (sintering time = 24 h), the bulk thermal expansion of CMZP decreased from $3.4 \times 10^{-6}/^\circ\text{C}$ to $-2.11 \times 10^{-6}/^\circ\text{C}$ while the grain size increased from 2 μm to 30 μm . Similarly, an increase in grain size from 5 to 12 μm was observed with longer sintering times (sintering temperature = 1235°C) while the bulk thermal expansion coefficient decreased to $0.122 \times 10^{-6}/^\circ\text{C}$ as illustrated in Figure 23. Scanning electron micrographs of the microstructure revealed the presence of a glassy phase within the grain boundaries and microcracks as shown in Figure 24. The decrease in thermal expansion with increased sintering time and temperature may be attributed to microcracking and the glassy phase which appears to be a zinc phosphate.

Slip Cast CMZP

Techniques for slip casting C6M4ZP were developed. CMZP powder synthesized by either solid state reaction methods or sol-gel techniques, an organic binder, and water were mixed in a ball mill. Additional water and HCl was added to form a slip, then the CMZP was cast into either flat plate or cup molds. The green bodies were dried at room temperature and at 100°C for 10 h, then fired at 1200°C for 24 h. The resulting ceramics exhibited densities of about 90% of theoretical.

Hot Pressed CMZP

Dr. Michael Haselkorn, Caterpillar Inc., hot pressed disks of amorphous sol-gel derived C6M4ZP for 0.25 to 4 h at temperatures of 1240-1350°C in either Ar or vacuum (Table 18). The C6M4ZP disks were easily sintered to

Figure 22. Effect of sintering temperature (time: 24 h) on grain size and CTE of C6M4ZP formed by sol-gel method I

Figure 23. Effect of sintering time on grain size of C6M4ZP derived using sol-gel method I

Figure 24. Microstructure on as-sintered surfaces of C6M4ZP synthesized by the sol-gel technique then sintered at (a) 1150°C for 24 h, (b) 1235°C for 24 h, (c) 1235°C for 72 h, and (d) 1300°C for 24 h

(c)

(d)

Table 18. Effect of Hot Pressing Conditions on Strength
and CTE of C6M4ZP

<u>RUN</u>	<u>Heating Ramp (°C/min)</u>	<u>Soak Temperature & Time (°C, min)</u>	<u>Ram Pressure (psi)</u>	<u>CTE (10⁻⁶/°C)</u>	<u>MOR (MPa)</u>
7	5	1290, 240	5600	3.4	136.3±21
15	10 to 400 20 to soak	1250, 15	5600 at 500C	2.8	115±11
6	5	1240, 240	5600 in Argon	3.3	107±15
4	5	1240, 240	5600	3.4	101±15
10	5 to 400 14 to soak	1260, 120	5600 at 840	3.1	97±8
9	5 to 400 14 to soak	1240, 90	5600 at 825	3.7	96±7
16	10 to 400 20 to soak	1250, 15	8400 at 600	3.3	87±11
14	10 to 400 20 to soak	1250, 30	5600 at 600	2.9	6±10
11	5 to 400 14 to soak	1260, 90	5600 at 800	2.9	78±8
12	5 to 400 14 to soak	1280, 30	5600 at 800	2.8	78±10
17	10 to 400	1260, 15	8400	2.8	73±8

densities greater than 98% of theoretical indicative of good fabricability. The flexural strength, elastic modulus, and thermal expansion (CTE) of samples cut from the hot pressed disks were determined. The microstructure and fracture surfaces of the samples were examined using both optical and scanning electron microscopy to determine if there was any correlation with the hot pressing conditions and/or the moduli of rupture (MOR) values. It was observed that a 5°C/min heating ramp to a temperature of 1240-1290°C and an applied ram pressure of 5600 psi at the soak temperature leads to flexural strengths of greater than 100 MPa with elastic moduli of approximately 100 GPa. The maximum average modulus of rupture obtained was 136 MPa.

Fracture surfaces of the strongest samples exhibited negligible porosity and microcracking as shown in Figure 25a. To determine the grain size, a fracture surface from pressing run 7 was etched with HF (Figure 25b). The mean grain size is approximately 2 μm with angular boundaries indicative of liquid phase sintering and/or grain growth processes. Examination of broken pieces from the edge of the pressed disk confirm the presence of a liquid phase on the grain boundaries (Figure 26). The fracture surfaces of bars having the lowest strengths exhibited microcracks parallel to the pressing direction as shown in Figure 27. The grain morphology of the weakest samples as revealed by HF etching consisted of an agglomerated structure with what appears to be both very small and large grains as shown in Figure 28.

Thermal expansion coefficients of hot pressed C6M4ZP vary from 2.8 to $3.4 \times 10^{-6}/^{\circ}\text{C}$ averaged over a temperature range of 30 - 1000°C. The positive expansion values are consistent with the small grain sizes (2 μm or less) observed in all samples.

Mechanical Properties of CMZP

Based on optimization studies, C6M4ZP samples for evaluation of mechanical properties were hot pressed with a heating rate of 5°C/min to 1250°C then a pressure of 5600 psi applied at 1250°C for 4 h. Bulk density of the hot pressed specimens averaged 3.175 g/cc which is greater than 99% of theoretical density as measured by ASTM C20-87. The modulus of rupture (MOR) or flexural strength was determined at room temperature using Military

Figure 25. Microstructure of C6M4ZP hot pressed at 1290°C for 240 min (Run 7) (a) Fracture surface (b) Etched

Figure 26. Etched microstructure of C6M4ZP at the edge of disc from hot pressing Run 7

Figure 27. Fracture surface of bar from hot pressing Run 17

Figure 28. Etched microstructure of bars from hot pressing Run 17

Standard 1942 B in four point bending. The same specification was also applied to the high temperature tests at 850°C, 1050°C, and 1250°C. The strength measurements were made at HTML, ORNL. The average room temperature MOR was 125 MPa with a Weibull modulus of 10.7, at 850°C, the strength decreased to 118 MPa and at 1050°C was 90 MPa. At 1250°C, C6M4ZP exhibited significant creep and the MOR could not be determined. These results are shown in Table 19.

Table 19. Flexural Strength and Elastic Modulus of C6M4ZP

Temp <u>°C</u>	MOR <u>MPa</u>	Elastic Modulus <u>GPa</u>	<u>No. of Samples</u>
23	125±12*	118±7*	19
850	118±22	69±4	3
1050	90±1	78±1	3
1250	all samples crept		2

*sample standard deviation

To verify the static elastic modulus calculated from the room temperature flexure test, the dynamic modulus (ultrasonic pulse-echo technique) was determined on six of the hot pressed C6M4ZP disks before machining MOR bars from them. The dynamic modulus was measured as 114 GPa with a sample standard deviation of 7.

The fracture toughness of hot pressed C6M4ZP was also determined using the indentation strength method⁴. Six samples were tested. Three Vickers indents 5 mm apart were made on the tensile surface of each bar using a load of 9.8 KN. The fracture toughness was determined to be 1.27 MPa (m)^{1/2}.

Expansion Hysteresis of CMZP

The effect of thermal cycling on the thermal expansion of C6M4ZP was examined. Hot pressed C6M4ZP were cycled from room temperature to 1000°C ten times. No significant change in expansion after cycling and no significant hysteresis were observed as shown in Figure 29. The average coefficient of thermal expansion on heating from room temperature to 1000°C was $3.20 \times 10^{-6}/^{\circ}\text{C}$ and on cooling was $3.71 \times 10^{-6}/^{\circ}\text{C}$.

RCZP

$(\text{Rb}_{1-x}\text{Cs}_x)\text{Zr}_2(\text{PO}_4)_3$ (RCZP) compositions were evaluated as candidate low expansion ceramics for use in advanced heat engines. RCZP powders were synthesized using a sol-gel technique similar to one previously used for preparing CMZP powders. Gels were prepared using both basic (pH 9) and acidic (pH 2) conditions. By calcining the sol-gel products at about 950°C, single phase crystalline RCZP powders could be formed regardless of the process pH conditions. Densities greater than 98% of theoretical were achieved by hot pressing the sol-gel synthesized powders at 1200°C and 14 MPa for 5 h. The bulk expansion coefficients of the hot pressed samples varied from 0.0 to $0.8 \times 10^{-7}/^{\circ}\text{C}$ (30 to 1000°C).

For RCZP, it was previously shown that the thermal expansion was non-linear with increasing temperature. The effect of the sintering process on this non-linearity was studied by controlling the heating and cooling rates of the compositions ($x = 0.0 - 1.0$ by 0.1 increments). It was found that the non-linear expansion is not affected by rapid heating or cooling. No direct correlation between the grain size and the expansion was observed for samples prepared by sol-gel synthesis, cold pressing, then sintering.

The thermal stabilities of RCZP ceramics were examined after long term heat treatments in air at temperatures up to 1300°C. The compositions exhibited decomposition, evidenced by the formation of ZrP_2O_7 , $\text{Zr}_2\text{P}_2\text{O}_9$, and ZrO_2 after treatments above 1000°C for 8-40 h. In particular, compositions where $x = 0.4, 0.9$, and 1.0 showed considerable instability, which was manifested by the presence of either zirconium phosphate or an unidentified

Figure 29. Effect of thermal cycling on relative expansion of C6M4ZP hot pressed at 1280°C for 2 hours with 5600 psi

phase. The remaining compositions showed no decomposition but contained secondary phases of zirconia and $\text{Zr}_2\text{P}_2\text{O}_9$.

The phase stability was also investigated using a weight loss scheme in which samples were weighed after each repeated heating period. Compositions where $x = 0.0, 0.5$, and 1.0 were tested. The heat treatment schedule consisted of a 3 h period at 1000°C followed by ten 4 h heating periods at 1250°C . Sample weight and XRD data were obtained after each heating time. The Rb composition ($x = 0.0$) exhibited better stability than Cs-containing samples with a weight retention of 94.7%, while the Cs-containing compositions exhibited a retention of approximately 91%.

Due to the instability below 1250°C , investigation of the RCZP materials were discontinued.

SiC Reinforced C6M4ZP Composites

To produce high density composites, powders of C6M4ZP were made using a variety of sol-gel techniques. Powders derived by one of the sol-gel methods studied were successfully transformed into single-phase crystalline C6M4ZP by firing at 1250°C for 24 h. The technique used involves a colloidal suspension made by adding NH_4OH to a mixture of solutions of $\text{ZrO}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$, and $\text{NH}_4\text{H}_2\text{PO}_4$ until a pH of 8-9 is reached. The suspension is dried at $40\text{-}60^\circ\text{C}$ while being stirred, dried at 110°C , and then calcined at 350°C for 10 h.

Composites made of 5 and 10 vol% chopped NICALON-SiC fibers in C6M4ZP powders derived by sol-gel techniques were hot pressed either in air, nitrogen, or argon. Initial studies indicated that hot pressing in air at 1200°C for 8 h at 18.4 MPa followed by annealing at 1200°C for 24 h yielded densities greater than 97% of theoretical for disks 50 mm in diameter by 3 mm thick. By increasing the pressure to 27 MPa and using an inert atmosphere, composites having densities greater than 98% of theoretical were formed by hot pressing at 1200°C for 6 h.

Examination of the microstructures of these composites using scanning electron microscopy showed a mean grain size of approximately $10\text{ }\mu\text{m}$. Composites that were hot pressed in air exhibited some bonding between the

fiber and the matrix and the fiber surfaces appeared to be rough. The composites pressed in an inert atmosphere exhibited fiber/matrix debonding and smooth fiber surfaces.

The bulk thermal expansion coefficients of the composites containing 5 and 10 vol% fibers ($-6.0 \times 10^{-7}/^{\circ}\text{C}$ and $-1.8 \times 10^{-7}/^{\circ}\text{C}$, respectively) are slightly negative compared to that of C6M4ZP.

The effects of aging heat treatments and fiber volume fraction on the bulk thermal expansion of chopped Nicalon-SiC fiber-reinforced C6M4ZP were also investigated. A composite containing 5 vol% chopped fibers was hot pressed in air at 1220°C at 14 MPa pressure for 6 h, then aged in air at 1200°C for 4 h without pressure. The average bulk coefficient of thermal expansion (CTE) of the composite was $-2.0 \times 10^{-7}/^{\circ}\text{C}$. Another composite containing 5 vol% fibers was hot pressed in N_2 under similar conditions, then aged in N_2 at 1220°C for 20 h. This sample had a bulk CTE of $-8.0 \times 10^{-7}/^{\circ}\text{C}$. Preliminary results indicate that the hot pressing atmosphere has no significant effect on CTE and, similar to previous observations for monolithic C6M4ZP, the CTE becomes more negative with aging. It is noted that both these composites had densities greater than 96% of theoretical.

Composites containing 20 vol% chopped fibers were prepared by hot pressing in air or Ar at 1230°C and 30 MPa pressure for 3 h. Densities of these samples, 90 - 92% of theoretical, were lower than those of composites containing lower fiber volume fractions. The bulk CTE of the high fiber volume fraction composites was $14 \times 10^{-7}/^{\circ}\text{C}$, independent of hot pressing atmosphere.

The nature of the fiber-matrix interface is known to have a significant effect on the toughness-related properties of ceramic composites. The chemistry of the interface between Nicalon-SiC fibers and a C6M4ZP matrix was characterized thermodynamically using SOLGASMIX-PV, a computer program for calculating equilibrium relationships in complex chemical systems.⁵ Since the C6M4ZP composites are currently produced in the laboratory by hot pressing at approximately 1230°C in either air or Ar atmospheres, these conditions were used in the thermodynamic calculations.

The results of the SOLGASMIX analysis for these conditions indicate that C6M4ZP reacts with SiC in either air or Ar to form $\text{Ca}_{3-x}\text{MgSi}_2\text{O}_{8-x}$ (x may be 0, 1, or 2) and possibly MgO , ZrP_2O_7 , $\text{Zr}_2\text{P}_2\text{O}_9$, ZrSiO_4 , or SiO_2 , depending on

system conditions. Even when SiO_2 is assumed present with SiC and CMZP, it is noted that the SiC is oxidized even in an Ar atmosphere suggesting that oxygen may be provided to the interface by the C6M4ZP.

Energy Dispersive X-ray Analysis (EDX) was used to examine the hot pressed C6M4ZP composites to determine the Si, Ca, Mg, Zr, and P contents in both the fiber surfaces and the interfacial area of the matrix exposed by fiber removal (matrix trough). The EDX results indicate that the Si content in the matrix trough of the sample pressed in air is significantly higher than that of the sample pressed in Ar. Since Si is not likely to exist in the form of SiC in the matrix, the high Si content in the trough indicates the possible oxidation of SiC fibers when the composite is pressed in air.

The fiber-matrix interface of C6M4ZP composites that were hot pressed in air and argon are shown in Figures 30 and 31, respectively. The composite pressed in air exhibited some bonding between the fiber and matrix and the fiber surfaces appeared to be rough, probably due to SiO_2 formation. The composites pressed in argon exhibited fiber/matrix debonding and smooth fiber surfaces.

The chemistry of the fiber/matrix interface of Nicalon-SiC/C6M4ZP composites hot pressed in air or in an O_2 -deficit atmosphere was further investigated using Auger Electron Scanning (AES) microscopy. An AES microscope (Perkin Elmer Model 610) with a scanning beam size of $3\text{ }\mu\text{m}$ was used to examine both the fiber surfaces and troughs in the matrix where fibers had been removed. The amount of C and Si in the matrix trough for the sample pressed in air was higher than in the sample pressed in Ar as shown in Table 20. Since Si and C are not likely to exist in the form of SiC in the matrix, the presence of Si and C confirms that C6M4ZP reacts with SiC in either Ar or air. This reaction was indicated by energy dispersive x-ray analyses of the fiber surface and trough and by calculations of thermodynamic equilibrium using SOLGASMIX-PV.

Figure 30. Nicalon-SiC/C6M4ZP composite hot pressed in air

Figure 31. Nicalon/SiC C6M4ZP composite hot pressed in Ar

Table 20. AES Analysis of Fiber Surface and Matrix Trough

<u>Elements</u>	Hot pressed in air (at%)		Hot pressed in Ar (at%)	
	<u>Fiber</u>	<u>Trough</u>	<u>Fiber</u>	<u>Trough</u>
C	13.7	9.2	11.2	6.4
O	39.2	45.9	35.8	38.1
Si	17.3	15.9	16.7	9.9
Ca	4.0	2.4	2.7	1.7
Zr	4.3	9.3	5.2	17.6
P	1.7	5.0	2.6	16.4

The effects of fiber volume fraction and processing on the flexure strength of C6M4ZP reinforced with either chopped Nicalon-SiC fibers or SiC whiskers was investigated. The C6M4ZP used for this study was prepared by sol-gel synthesis.

Disks 50 mm in diameter were hot pressed in air, N₂, or Ar at the temperature and pressures indicated on Table 21. Three to five specimens approximately 25 mm long were cut from the center of each disk then ground smooth and the edges chamfered. The specimens were broken in three point bending with a span of 20 mm and a crosshead speed of 0.2 mm/min using an ATS universal testing machine with a load capacity of 225 Kg. No significant increase in strength was observed by increasing the fiber content from 5 to 10 vol%. Similar to the samples hot pressed in air, no increase in strength was observed for the samples hot pressed in an inert atmosphere by increasing the fiber content from 5 to 10 vol%. These strengths are significantly less than that of hot pressed unreinforced C6M4ZP (approximately 91 MPa).

Table 21. Fracture Strength of Composites Hot Pressed in Air

<u>Fiber Content (vol%)</u>	<u>Processing conditions (Temp./Pressure,Time)</u>	<u>Density (% Theoretical)</u>	<u>MOR (MPa)</u>
5	1210°C/18 MPa, 2 h	97	49.6 ± 9.5
10	1210°C/18 MPa, 2 h	97	50.4 ± 10.6
20	1210°C/18 MPa, 2 h	93	61.2 ± 6.6
20	1210°C/30 MPa, 3 h	98	91.3 ± 7.1

The 20% sample pressed at 18 MPa for 2 h exhibited a lower density because one of the supporting bricks in the hot press failed. The strength of the composites is significantly increased by adding up to 20 vol% chopped fibers and with higher densities as achieved with higher pressure and temperature during pressing.

A SiC whisker/C6M4ZP composite sample containing 20 wt% of SiC whiskers HIPed at 1250°C under 103 MPa (15000 psi) for 10 minutes exhibited a relative density of 92%. Another sample with the same composition was HIPed using the same temperature and pressure conditions but with a longer time of 1 h yielding a density of 94% of theoretical. The coefficient of thermal expansion of these two samples is $2.6 \times 10^{-6}/^{\circ}\text{C}$, which is nearly the value of $2.5 \times 10^{-6}/^{\circ}\text{C}$ for the hot pressed CMZP composite sample containing 9 wt% (10 vol%) of SiC whiskers reported previously.

Sol-gel derived C6M4ZP powders with 10 vol% SiC whiskers were turbomilled by Dr. Dale Wittmer at Southern Illinois University. A disk of 50 mm in diameter was then made by hot pressing the C6M4ZP powder-SiC whisker mixture with 1.5 wt% ZnO as sintering aid. The processing conditions are listed on Table 22. Densities greater than 97% of theoretical were achieved in the central part of the disk. The average flexure strength of four bars from the center of the composite disk was 141.3 (± 11) MPa measured in three point bending. This strength is much larger than that achieved for chopped fiber

reinforced C6M4ZP (Table 22) and hot pressed unreinforced C6M4ZP (approximately 91 MPa). The microstructure of the fracture surface is shown in Figure 32 which exhibits fine grain size, whisker pull outs, and low porosity.

Table 22. Flexure Strength of SiC/CMZP Composites

Reinforcement Content (vol %)	Processing Conditions (Temp./Pressure, Time)	Density (% Theoretical)	MOR (MPa)
5 (fiber)	1210°C/18 MPa, 8h in N ₂	98	47.7±10
10 (fiber)	1210°C/27 MPa, 6h in Ar	98	48.3±12
10 (whisker)	1230°C/30 MPa, 4h in Ar	97	141.3±11

The fracture toughness of hot pressed monolithic C6M4ZP and 10 vol% SiC whisker/C6M4ZP was evaluated using the indentation technique. The sample tested was hot pressed at 1230°C under 30 MPa for 4 hours. The K_{Ic} values were calculated using the following equation developed by Antis, et. al.⁶ Indents were made on the surfaces parallel and perpendicular to the pressure direction. The hardness was measured using a Vicker's indenter with a 9.81 N load for 10 seconds. The monolithic sample exhibited a hardness of 478 VHN perpendicular to the hot pressing axis and 462 parallel, while whisker-reinforced C6M4ZP exhibited values of 451 VHN and 398 VHN, respectively. The average K_{Ic} (8 indents) on the surface parallel to pressure direction was 2.41 MPa(m^{1/2}) ($\pm$ 0.46) and on the surface perpendicular, the average was 1.52($\pm$ 0.12) MPa(m^{1/2}). The K_{Ic} values are higher than the corresponding values determined for hot pressed monolithic C6M4ZP (1.24 MPa(m^{1/2}), parallel and 1.35 MPa(m^{1/2}), perpendicular). Optical micrographs of the samples indicate that the toughening mechanism was crack deflection.

The development of hot isostatic pressing (HIP) techniques for the densification of SiC whisker reinforced C6M4ZP were investigated. Sol-gel derived C6M4ZP powders were mixed with SiC whiskers in water and stirred constantly for 24 h to achieve a high homogeneity. The powder-whisker

Figure 32. Fracture surface of whisker reinforced C6M4ZP

mixtures were next dried, then cold-pressed into billets. The billets were fired at 1000°C for 6 h to eliminate volatiles and to consolidate the mixture. Next, billets were encapsulated in Pyrex glass tubes under vacuum at temperatures between 600 and 800°C, then slowly cooled to room temperature to avoid cracking the glass.

Mechanical properties of SiC whisker reinforced C6M4ZP composites, including flexural strength and Young's modulus at both room temperature and 858±1°C, fracture toughness and R-curve behavior at room temperature were evaluated at ORNL HTML. The composite samples were hipped at 1050°C at 103 MPa for 0.25 hours, then machined into MOR bars with the prospective tensile surface being polished using 900 grit paper, and tested according to Military Specification 1942 B in four point bending.

For room temperature bending tests, an Instron Model 6027 machine and a set of stainless steel 20/40mm fixture were used. For high temperature bending tests, an Instron Model 6027 machine with an ATS 3320 furnace and a Pneumatic testing machine with a CM furnace were used. Fixtures for high temperature tests were made of alumina with SiC pins.

Flexural strength of the composites was measured at room temperature and 858±1°C. For high temperature testing, the specimens were heated up from room temperature to the testing temperature at a rate of 25-30°C/min. After the furnace temperature reached the setting point, the system was held at that temperature for at least 5 minutes before starting loading so as to achieve a temperature homogeneity in specimens.

The flexural strength of the composite with 20 vol% whiskers was measured to be 155 MPa as the average of three MOR bars. For the composite with 30 vol% whiskers, the value was 175 MPa, which was also the average of bars. The flexural strengths and Young's moduli of the composites measured at 858±1°C and at room temperature are listed on Table 23. At room temperature, for the composite with 20 vol% SiC whisker content, the Young's modulus was calculated as 134 GPa (average of 4 specimens); for 30 vol% whisker content, the value was 148 GPa (3 specimens).

It can be seen from the Table 23 that at 858°C, the composites have a higher flexural strength but a lower Young's modulus than those at room

temperature. Correspondingly, the deflection of the tested MOR bars at 858°C was found to be significantly larger.

Table 23. Temperature effects on flexural strength and Young's modulus of SiCw/C6M4ZP composites

<u>Temperature</u>	<u>Flexural Strength (MPa)</u>		<u>E (GPa)</u>	
	<u>20w</u>	<u>30w</u>	<u>20w</u>	<u>30w</u>
RT	122	131	134	148
858°C	155	75	175	88

In Figure 33, average bending force exerted on the MOR bars of the composites at breaking are plotted against average deflection of the bars. For the composites containing 20 and 30 vol% SiC whiskers, the area under the force-deflection curve, which is a measure of fracture energy, is obviously larger at 858°C than that at room temperature. This may suggest that at this temperature, the composites have a higher fracture resistance since more energy is needed to break them. More study, such as R-curve behavior of the composites at 858°C is needed before a solid conclusion can be made in this respect.

Fracture toughness and R-Curve behavior of the composites were assessed using indentation-flexural strength technique. The indentation loads used in the tests were 26 ± 1 , 34 ± 1 , 44 ± 1 , and 54 ± 1 Newtons for the composite containing 20 vol% of whiskers and 26 ± 1 , 34 ± 1 , 44 ± 1 , 54 ± 1 , and 88 ± 1 Newtons for the composite with 30 vol% of whiskers.

The calculated K_{IC} values⁷ and other parameters used in the calculations are listed in Table 24. The results indicate that the fracture toughness of the composites increases with the whisker content. In Figure 34, K_{IC} values are plotted against c^* , it can be seen that the composites show R-curve behavior.

Figure 33. Plot of bending force against deflection of SiCw/C6M4ZP MOR bars

Figure 34. Plot of K_{IC} of SiCw/C6M4ZP composites against crack length

Table 24. Fracture toughness of SiCw/C6M4ZP composites and parameters used for calculations

Ind. Load <u>(N)</u>	c^* <u>(μm)</u>	S_f <u>(MPa)</u>	K_{Ic} <u>(MPa$\cdot\text{m}^{1/2}$)</u>	Y <u>_____</u>	# of Bars <u>tested</u>
20 vol% whisker					
26	125	84.5	1.198	1.268	1
34	175	79.8	1.320	1.260	1
44	196	77.8	1.360	1.256	4
54	232	74.2	1.407	1.253	4
30 vol% whisker					
26	139	94.8	1.410	1.266	3
34	154	93.4	1.463	1.263	3
44	188	84.9	1.521	1.255	3
54	230	82.3	1.555	1.251	4
88	306	75.2	1.626	1.238	3

R-curve behavior of the composites was also evaluated by presenting the fracture resistance, K_R , of the composites as a function of crack extension, c , to a fractional power.⁸

$$K_R = kc^m \quad (\text{MPa}\cdot\text{m}^{1/2}) \quad (1)$$

Using the above mentioned indentation load, Y value, and flexural strength data, k and m values that determined K_R of the composites were calculated as 11.847 and 0.214 for 20 vol% whisker content, 9.25 and 0.162 for 30 vol% whisker content, respectively. The corresponding unit of crack length, c , should be meters when using these values to calculate K_R .

The fracture resistances of the composites are plotted against crack lengths in Figure 35. Again, the plots indicate that the C6M4ZP composites show an obvious R-curve behavior. Both the graphs show that a higher whisker content (30 vol%) results in a higher fracture resistance over a lower whisker content (20 vol%). From Figure 34, the upper-bound saturation fracture toughness, K_{C_u} , at large crack lengths, and the lower-bound fracture toughness, K_{C_l} , corresponding to a preexistent-crack-free state, can be estimated as 2.10 and 1.20 $\text{MPa}\cdot\text{m}^{1/2}$ for 20 vol% whisker content, and 2.60 and 1.60 $\text{MPa}\cdot\text{m}^{1/2}$ for 30 vol% whisker content, respectively.

On the other hand, fracture toughness of the composites was also evaluated by immediately measuring indent size and crack length after each indentation and then, using the Antis equation⁶.

The K_{Ic} values obtained through this approach were 2.20 ± 0.353 $\text{MPa}\cdot\text{m}^{1/2}$ for 20 vol% whisker content and 2.78 ± 0.470 $\text{MPa}\cdot\text{m}^{1/2}$ for 30 vol% whisker content. These K_{Ic} values are correspondingly close to the upper-bound K_R values derived from the above-mentioned R-curves. While the K_{Ic} values obtained using Equation 2 are similar to the corresponding lower-bound K_R values.

In Situ Whisker Reinforced NZP

A technique has been developed whereby CMZP is reinforced by $(\text{Nb}_x\text{Ca}_{1-x})\text{Zr}(\text{PO}_4)_5$ [NbCZP] whiskers grown in situ during sintering. Whiskers are formed from NbCZP which is synthesized using the same sol-gel techniques as CMZP with Nb_2O_5 replacing the magnesia precursor. NbCZP (10-50 wt %) and C6M4ZP powders were blended then cold pressed and sintered at 1000-1200°C for 4 - 72 h. No sintering aid was used. A typical microstructure of the NbCZP/C6M4ZP composite exhibited many pores as shown in Figure 36. Whiskers were usually found in or adjacent to a pore in the composite.

Energy dispersive x-ray analysis (EDX) was used to examine the elemental distribution of a typical whisker and the grains nearby. The analysis indicates equal amounts of O, P, and Ca in both the whisker and grains. The peaks for Nb and Zr are hidden by the dominant P peak; no Mg is present in either the whisker or grains. The loss of Mg is still under investigation.

Figure 35. Plot of K_R of SiCw/C6M4ZP composites against crack length

Figure 36. Whisker formed in-situ in 50% NbCZP/C6M4ZP
sintered at 1150°C for 24 h

Five bars of 50 wt% NbCZP/C6M4ZP were cold pressed and sintered. Prior to mixing the sol-gel derived powders, the NbCZP was calcined at 600°C for 10 h to promote whisker growth. The bars were 4 x 5 x 50 mm then broken in four point bending. The MOR was 12.4 MPa $\pm$ 4 (1 σ) and the elastic modulus was 24.3 GPa ($\pm$ 11). The density of the samples was 2.18 gm/cc.

Lightweight Ceramics

Two techniques for making lightweight CMZP ceramics have been developed. In one technique, a polymer foam is either coated or saturated with a slurry of CMZP powder, then sintered to yield a structure with pore sizes of 150 to 230 μ m. In the second technique, a polymer powder is blended with CMZP powders and binders, pressed, then sintered to form a lightweight ceramic with pore sizes of 30-50 μ m (approximately the polymer powder particle size).

The mechanical properties of the lightweight ceramics and the effects of processing parameters on these properties were studied. Samples of lightweight ceramics were tested in uniaxial tension using an Instron Model 4202 universal test machine with a 4 kN capacity to determine the strengths and elastic moduli. The specimens were epoxied to aluminum stubs which were then attached to the testing machine. The tensile strength of the lightweight ceramics was found to increase with density and to be independent of composition as shown in Figure 37. Lightweight ceramics made by the polymer powder method appear to have higher tensile strength than those made by the polymer foam method.

Because an extensometer could not be attached to specimens without inducing damage, the modulus was determined by subtracting the stiffness of the grips epoxied together from the stiffness of the sample determined from the stress vs cross head displacement of each test. There appeared to be no significant difference in the elastic modulus due to processing technique. The elastic modulus, however, tends to increase with Mg content. The modulus also increases with density as shown in Figure 38. The amount of sintering aid (ZnO) appears to have an insignificant effect on the thermal expansion and mechanical properties.

Figure 37. Tensile strength of lightweight ceramics as a function of density

Figure 38. Elastic modulus of lightweight ceramics as a function of density

The flexural strength of lightweight $(\text{Ca}_{1-x}\text{Mg}_x)\text{Zr}_4(\text{PO}_4)_6$ ceramics where $x = 0.0-0.3$ are shown in Figure 39 as a function of relative density. Included in the figure is the strength of open cell ZrO_2 . As shown, the strength determined by 3-point bending compares favorably with that of open cell ZrO_2 . The strengths were independent of composition.

The room temperature compressive strength of lightweight $(\text{Ca}_{1-x}\text{Mg}_x)\text{Zr}_4(\text{PO}_4)_6$ ceramics was measured. Figure 40 shows the strength of lightweight CMZP as compared to lightweight ZrO_2 -4%MgO, a conventional thermal barrier material. Both materials have relative densities varying between 0.2 and 0.7. The compressive strength of $(\text{Ca,Mg})\text{Zr}_4(\text{PO}_4)_6$ is strongly related to the density. Furthermore, it appears to be independent of the composition as noted previously for MOR and tensile strengths. The compressive strength compares favorably with that of partially-stabilized zirconia.

The thermal shock resistance of lightweight CMZP made by the polymer powder method was investigated. As shown in Figure 41, lightweight ceramics with relative densities of 0.87 and 0.54 exhibit no significant strength losses following air quenching from any temperature up to 1550°C . The addition of ZnO, a sintering aid, increased the modulus of rupture and did not appear to affect the thermal shock resistance.

Corrosion of lightweight $(\text{Ca}_{1-x}\text{Mg}_x)\text{Zr}_4(\text{PO}_4)_6$ ($x = 0.1-0.5$) immersed in aqueous HCl ($N = 12.1$) and HNO_3 ($N = 15.8$) was examined. After exposure at room temperature for over 1000 h, weight losses of 1-3% were observed. Results of XRD analyses revealed no evidence of decomposition indicating that the lightweight ceramics have excellent acid-corrosion resistance.

An analysis of the permeability of the lightweight ceramics indicates that material made by the polymer foam method has primarily an open cell structure while the ceramic made by the powder method has a closed cell structure. The relationship between permeability and both processing and relative density is shown in Figure 42.

Lightweight CMZP ceramics with smaller pore sizes were made by coating a polymer substrate using sol-gel techniques. The reticulated polymers were coated with the gel then dried, pyrolyzed, and sintered yielding a lightweight ceramic with open cells smaller than $200\text{ }\mu\text{m}$. The struts between

Figure 39. Flexural strength of lightweight CMZP as a function of relative density

Figure 40. Compressive strength as a function of bulk density of lightweight CMZP and stabilized zirconia

Figure 41. Thermal shock resistance of lightweight CMZP

Figure 42. Effect of processing method on the permeability of lightweight ceramics

Figure 43. Lightweight open cell CMZP ceramic

Figure 44. Micrograph of dense protective layer on the surface of Si_3N_4 coated with CMZP after sodium corrosion

cells are hollow due to pyrolysis of the polymer substrate and have wall thicknesses between 40 and 100 μm as shown in Figure 43.

CMZP Coatings

To improve the alkali corrosion resistance of ceramics such as Si_3N_4 and SiC , CMZP coatings derived by both organic and inorganic sol-gel techniques have been investigated. Films of CMZP were put on Si_3N_4 substrates which were then covered with an aqueous solution of NaCO_3 at room temperature then heated to 1000°C and held for 40 h. The room temperature flexural strength of as-received, coated, and corroded Si_3N_4 was measured according to Military Specification 1942B. The flexural strengths reported are an average of five specimens. Before alkali exposure, both the coated and uncoated Si_3N_4 exhibited an average flexural strength of 595 MPa. After exposure, the average strength of the coated samples increased to 669 MPa while the uncoated samples exhibited an average strength of 573 MPa. It is believed that CMZP reacts with the protective SiO_2 film on Si_3N_4 to form a continuous reaction layer that minimizes corrosion. A scanning electron micrograph of the dense protective layer is shown in Figure 44.

β -EUCRYPTITE- AlPO_4 SYSTEM

Glass-ceramics in the modified AlPO_4 - β -eucryptite system were chosen for further study based on the results shown in Part I of this study because of the ease of manufacture, relatively good strength and toughness, good thermal shock resistance, and chemical stability. As was discussed previously, the thermal expansion coefficient of modified β -eucryptite can be controlled by creating a solid solution phase containing aluminum phosphate and replacing some of the lithia with either magnesia or lime forming $(\text{Li}_{0.41}, \text{Mg}_{0.035})\text{Al}(\text{Si}_{0.48}, \text{P}_{0.52})\text{O}_4$ or $(\text{Li}_{0.4}, \text{Ca}_{0.05})\text{Al}(\text{Si}_{0.75}, \text{P}_{0.5})\text{O}_{4.5}$, respectively. These modifications also lower the thermal expansion anisotropy which causes microcracking and is believed to be related to decreased corrosion resistance. During this study it was also discovered that whiskers could be grown in situ

during glass-ceramic heat treatment significantly improving the strength of modified β -eucryptite.

Processing

A process has been developed to form in-situ whiskers in modified β -eucryptite which improves the strength of the material while maintaining a near-zero coefficient of thermal expansion (CTE).

Modified β -eucryptite $(\text{Li}_{0.41}, \text{Mg}_{0.035})\text{Al}(\text{P}_{0.52}, \text{Si}_{0.48})\text{O}_4$ is prepared using a solid-state reaction method then mixed with up to 12 wt % of either TiO_2 or ZrO_2 and heated at 1600°C to form a glass. The glass melt is quenched in water, ground to a fine powder, then mixed with acetone to form a slurry which is poured into a mold. The acetone is drained leaving a compact. The compact is heat treated at 680°C to allow coalescence of the glass particles and then recrystallized at 1100°C . The resulting ceramic contains randomly oriented whiskers with an aspect ratio of approximately 30 as shown in Figure 45 for a sample containing 6 wt% TiO_2 . Electron microprobe analysis indicates that these acicular grains or whiskers are TiO_2 or ZrO_2 , depending on additive.

The presence of the whiskers in the modified β -eucryptite significantly improves the flexure strength as shown in Figure 46. With up to 12 wt % TiO_2 , the MOR determined using three point bending tests show an increase in strength by a factor of two to three times.

The presence of the TiO_2 whiskers also affects the thermal expansion behavior of the material. The bulk CTE averaged over 20°C to 1000° increases from $-7.0 \times 10^{-7}/^\circ\text{C}$ to $+2.8 \times 10^{-7}/^\circ\text{C}$ when the TiO_2 content is increased from 0 to 12 wt % as shown in Table 25. From the thermal expansion data it is seen that the incorporation of 8-10 wt% TiO_2 produces a β -eucryptite which exhibits a near zero CTE.

Additions of 2 wt% CaO to $(\text{Li}_{0.41}, \text{Mg}_{0.035})\text{Al}(\text{Si}_{0.48}, \text{P}_{0.52})\text{O}_4$ reduce microcrack formation during recrystallization. CaO appears to reduce the viscosity of the glass during recrystallization thus relieving the internal stresses induced by the volume change during the glass to glass-ceramic transformation. However, the melting temperature of recrystallized modified β -

Figure 45. Microstructure of modified β -eucryptite with 6 wt % TiO_2

Figure 46. Effect of TiO_2 content on the flexure strength of modified β -eucryptite

eucryptite was reduced to 1000°C as measured using differential thermal analysis (DTA).

Thus, one way to increase the melting temperature of the modified β -eucryptite is to add silica; hence, a new glass-ceramic which contains higher silica content,

Table 25. Effect of TiO_2 Content on CTE of Modified β -eucryptite

<u>TiO_2 content (wt%)</u>	<u>Average Bulk CTE (30-1000°C)</u>
0	$-7.0 \times 10^{-7}/^\circ\text{C}$
6	$-2.5 \times 10^{-7}/^\circ\text{C}$
8	$0.5 \times 10^{-7}/^\circ\text{C}$
10	$0.9 \times 10^{-7}/^\circ\text{C}$
12	$2.8 \times 10^{-7}/^\circ\text{C}$

$(\text{Li}_{0.4}, \text{Ca}_{0.05})\text{Al}(\text{Si}_{0.75}, \text{P}_{0.5})\text{O}_{4.5}$, was synthesized by the conventional glass-ceramic processing method. $(\text{Li}_{0.4}, \text{Ca}_{0.05})\text{Al}(\text{Si}_{0.75}, \text{P}_{0.5})\text{O}_{4.5}$ is a solid solution phase composed of 50 mol% $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ and 50 mol% AlPO_4 . This composition was obtained by solid state reaction of $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ and AlPO_4 at 1200°C for 100 hours. The resulting powder was mixed with 4 wt% TiO_2 (nucleating agent) and 2 wt% CaO by dry milling then melted at 1620°C. Next, the glass obtained was annealed at 550°C. The glass-ceramic was formed by heat treatments at 760°C and 1000°C. The melting temperature of $(\text{Li}_{0.4}, \text{Ca}_{0.05})\text{Al}(\text{Si}_{0.75}, \text{P}_{0.5})\text{O}_{4.5}$ is approximately 1200°C (measured using DTA). The resulting glass-ceramic has a grain size of 2-3 μm with no evidence of microcrack formation. Acicular grains of TiO_2 having an aspect ratio of 10-20 were formed during recrystallization and are shown in Figure 47. The bulk linear coefficient of thermal expansion of $(\text{Li}_{0.4}, \text{Ca}_{0.05})\text{Al}(\text{Si}_{0.75}, \text{P}_{0.5})\text{O}_{4.5}$ is $-4.3 \times 10^{-7}/^\circ\text{C}$ which is less negative than that of $(\text{Li}_{0.41}, \text{Mg}_{0.035})\text{Al}(\text{P}_{0.52}, \text{Si}_{0.48})\text{O}_4$ ($-7 \times 10^{-7}/^\circ\text{C}$). The strength of this ceramic is 134 (± 10) MPa measured in 4 point bending (20mm/40mm spans).

The effect of heat treatment conditions on the formation of in-situ whiskers and on the flexural strength of high silica modified β -eucryptite glass-

Figure 47. Fracture surface $(\text{Li}_{0.4}\text{Ca}_{0.05})\text{Al}(\text{Si}_{0.75}\text{P}_{0.5})\text{O}_{1.5}$

ceramics [96% $(\text{Li}_{0.4}, \text{Ca}_{0.05})\text{Al}(\text{Si}_{0.75}, \text{P}_{0.5})\text{O}_{4.5}$, 4% TiO_2] was investigated by making a glass and then heat treating it to form the crystalline phase. First, glass is formed by mixing $(\text{Li}_{0.4}, \text{Ca}_{0.05})\text{Al}(\text{Si}_{0.75}, \text{P}_{0.5})\text{O}_{4.5}$ synthesized by a solid state reaction process with 4 wt% TiO_2 , then melted at 1620°C , cast into a metal mold, and annealed. Differential thermal analysis (DTA) was used to determine the range of appropriate temperatures for nucleation and crystallization heat treatments. The DTA curve (Figure 48) exhibits a small endothermic peak at 670°C which corresponds to the glass transition temperature and an exothermic peak at 807°C associated with the crystallization of $(\text{Li}_{0.4}, \text{Ca}_{0.05})\text{Al}(\text{Si}_{0.75}, \text{P}_{0.5})\text{O}_{4.5}$.

The optimum nucleation treatment was determined by heating glass samples to temperatures from 670°C to 800°C for 0.5 h followed by a treatment at 950°C for 0.5 h to allow the nuclei to grow. The resulting glass-ceramic samples were examined using scanning electron microscopy (SEM) and found to exhibit grain sizes from 2 to $15\ \mu\text{m}$. The most uniform and small grains were formed at 740°C as shown in Figure 49.

To determine which crystal phases are formed, glasses were heated to 800°C - 1040°C for up to 20 h and the resulting crystallites identified using x-ray diffraction (XRD). As shown in Table 26, modified β -eucryptite begins to crystallize at 800°C and at higher temperatures, it is the dominant phase. Above 950°C , TiO_2 forms as a secondary phase. Figure 50 shows the microstructure of the glass crystallized at 1040°C for 20 hours in which randomly oriented acicular TiO_2 grains are found throughout the sample.

The elastic modulus, flexural strength, and toughness of high silica modified β -eucryptite glass-ceramics were found to depend upon the crystallization heat treatment as listed in Table 27. The samples were prepared by first nucleating the ceramic phase at 740°C for 0.5 h. These properties were measured using four point bending according to Military Standard 1942 B. The flexural strength varied from 67 MPa for the original glass to 134 MPa for the glass-ceramic which was heat treated at 1040°C for 20 h. It is believed that the increase in flexural strength with high temperature heat treatment results from the development of acicular TiO_2 grains. Similarly, the elastic modulus of the glass ceramic containing TiO_2 whiskers was approximately 40% greater than that of either the glass or glass-ceramic.

Figure 48. DTA curve of high silica modified β -eucryptite

Figure 49. Uniform nuclei formed in high silica modified β -eucryptite

Figure 50. Etched microstructure of high silica modified β -eucryptite

Table 26. Mechanical properties of AlPO_4 modified β -eucryptite glass ceramics

<u>Crystallization Heat Treatment</u>	<u>Elastic Modulus (GPa)</u>	<u>MOR (MPa)</u>	<u>K_{IC} (MPa$\cdot$1m)</u>
original glass	$62 \pm 9^*$	66 ± 5	1.1 ± 0.03
850°C , 2h**	67 ± 8	81 ± 12	--
950°C , 10h**	68 ± 13	72 ± 19	1.2 ± 0.07
1040°C , 20h***	85 ± 8	134 ± 13	1.6 ± 0.04

Table 27. Properties of high silica modified β -eucryptite glass-ceramics

<u>Crystallization Heat Treatment</u>	<u>Elastic Modulus (GPa)</u>	<u>MOR (MPa)</u>	<u>K_{IC} (MPa$\cdot$1m)</u>
original glass	62 ± 5	76 ± 3	3.2 ± 0.2
850°C , 2h**	67 ± 10	81 ± 9	--
950°C , 10h**	68 ± 10	72 ± 14	3.86 ± 0.6
1040°C , 20h***	85 ± 8	134 ± 10	4.93 ± 0.7

*95% confidence intervals shown

**Glass-ceramics without TiO_2 whisker precipitation

***Glass-ceramics with TiO_2 whisker precipitation

Techniques were developed to produce modified β -eucryptite using glass-ceramic techniques; however, severe microcracking occurred through the bulk due to thermal expansion mismatches between the parent glass and the recrystallized phase. To overcome this problem, two approaches have been taken. One is to create an in-situ whisker reinforced glass ceramic and the other is to reduce the viscosity of the glass during recrystallization and thus relieve the internal stresses induced by the volume change. The viscosity of the glass was reduced by adding 2 wt% CaO to the modified β -eucryptite. After heat treatment, the resulting material had no microcracks; however, the melting temperature was reduced to 1000°C making this material unacceptable for high temperature applications.

The corrosion resistance of modified β -eucryptite processed by conventional glass-ceramic techniques and by the newly developed method were compared to a commercial lithium aluminosilicate glass-ceramic (LAS) provided by Garrett Auxiliary Power Div., Allied Signal Corp., Phoenix, AZ. Samples were exposed to either aqueous HCl solutions at 25°C and 100°C or molten Na₂SO₄ at 1000°C and their weight change was monitored as a function of exposure time. When exposed to HCl, greater weight loss was recorded for the modified β -eucryptite than for the commercial LAS. With exposure to molten Na₂SO₄, both materials gained weight due to the formation of an alkali melt. The β -eucryptite material gained more weight than the commercial LAS. Scanning electron microscopy with EDX analysis of the exposed specimens revealed that the corrosion of the β -eucryptite produced by the conventional technique resulted from acid or molten salt penetrating the sample through the microcracks and removing AlPO₄ from the lattice. The β -eucryptite produced by the new method was corroded to a lesser extent because the AlPO₄ was removed from the sample surface only.

CONCLUSION AND RECOMMENDATIONS

The most promising new ceramic formulations identified for application in advanced heat engines were CMZP and modified β -eucryptite. In this study, the thermo-mechanical properties and fabricability of these ceramics were investigated.

The modified β -eucryptite ceramics were shown to lack corrosion resistance and hence will be limited in engine applications. A process was developed to form in-situ whisker reinforcement in glass-ceramics during conventional processing which significantly improves the strength of these ceramics. The application of this technology is still under investigation.

CMZP ceramics were easily fabricated by cold pressing/sintering, hot pressing, hot isostatic pressing, and slip casting using powders synthesized by sol gel or solid state reaction methods. The thermal expansion of CMZP was shown to vary from positive to negative depending on the grain size. The flexural strength of hot pressed CMZP is 125 MPa at room temperature decreasing to 90 MPa at 1050°C and flexural modulus of 118 and 78 GPa, respectively. This ceramic is stable at temperatures up to 1200°C and exhibits no expansion hysteresis on cycling to 1000°C. A technique for producing CMZP coatings on silicon carbide and silicon nitride were developed and preliminary results indicated that CMZP has good potential as an oxide barrier coating. CMZP is also readily reinforced with SiC whiskers or fibers, however, no improvement in strength/toughness was observed. Techniques for producing lightweight, porous CMZP were developed. The lightweight ceramic can be produced with either open or closed pores and exhibits properties similar to lightweight zirconia which is currently used in commercial applications.

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