Thermophysical Properties and Applications of [NZP] Materials

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(Low Thermal Expansion Ceramics)
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Applications of NZP Materials

**Diesel Engines**
- Exhaust Port Liners
- Manifold Insulation
- Particulate Trap
- Fire Deck

**Gas Turbine Engines**
- Heat Exchanger
- Housing
- Thermal Barrier Coatings
- Combustor Liners
Applications . . . (contd.)

**Power Generation**
- Catalytic Combustor Substrate
- *Hot Gas Filters*
- Heat Exchangers
- Burner Nozzles

**Metallurgical Operations**
- Molten Metal Handling (crucibles, nozzles, etc.)
- Braze and Carburizing Fixtures

**Space Systems**
- *Substrates for Optical Devices*

Additional applications include composite matrix, oxidation and thermal protection, etc.
[NZP] Background

- Basic Sodium Zirconium Phosphate [NZP] composition - NaZr$_2$P$_3$O$_{12}$
  - Discovered by Hagman and Kerkegaard in 1968.
  - Key to the unique properties of [NZP] materials is their crystal structure allows for the substitution by almost all of the alkali and alkaline earth metals.
Crystal Structure of [NZP]

- Three dimensional network (open) structure
- Corner-linked Polyhedra
- Ionic substitution flexibility
- Hence, can tailor composition to yield desired thermal and transport properties
- Structural rigidity/stability from the corner linking of polyhedra
[NZP] Materials: What do they offer?

- "Tailorable" thermal expansion
- Low thermal expansion anisotropy
- High thermal shock resistance
- High (>1800°C) melting temperature
- Amenable to various processes such as isostatic pressing, slip casting, gelcasting, tape casting, extrusion, injection molding, etc.
[NZP] Materials: Ionic Substitutions

PARTIAL IONIC SUBSTITUTIONS

Na$_{1+x}$Zr$_2$P$_3$-xSi$_x$O$_{12}$  Na$_{1+4x}$Zr$_2$-xP$_3$O$_{12}$
Ca$_{1-x}$ Mg$_x$Zr$_4$P$_6$O$_{24}$  Ca$_{1-x}$ Sr$_x$Zr$_4$P$_6$O$_{24}$  Ca$_{1+x}$ Ba$_x$Zr$_4$P$_6$O$_{24}$
Sr$_{1+x}$Zr$_2$P$_6$-2xSi$_x$O$_{24}$  Ba$_{1+x}$Zr$_4$P$_6$-2xSi$_x$O$_{24}$  Sr$_{1+4x}$Zr$_4$-xY$_x$P$_6$O$_{24}$
Na$_{1+x}$Zr$_2$-xCr$_x$P$_3$O$_{12}$  Na$_{1+x}$Zr$_2$-xIn$_x$P$_3$O$_{12}$  Na$_{1+x}$Zr$_2$-xYb$_x$P$_3$O$_{12}$
Na$_{1+x}$Zr$_2$Fe$_x$P$_3$O$_{12}$  Na$_{1+x}$Zr$_2$-xYb$_x$As$_3$O$_{12}$  Li$_{1+x}$Hf$_2$Nb$_x$P$_3$O$_{12}$
Li$_{1+x}$Hf$_2$Ta$_x$P$_3$O$_{12}$  Li$_{1+x}$Zr$_2$Nb$_x$P$_3$O$_{12}$  Li$_{1+x}$Zr$_2$Ta$_x$P$_3$O$_{12}$
Thermal Expansion and Anisotropy

Thermal expansion (a-axis)

Thermal expansion (c-axis)

Thermal expansion anisotropy

Bulk thermal expansion

Value of $x$ in $\text{Ba}_{1+x}\text{Zr}_4\text{P}_{6-2x}\text{Si}_2\text{O}_{24}$
Bulk Thermal Expansion

\[ \Delta L/L (\text{ppm}) \]

Temperature (°C)

Atmosphere: Room Air
Heating/Cooling Rate: 3°C/min

\[ \text{BS0, BS17, BS25, BS37.5, BS50} \]

\[ \text{Ba}_{1+x} \text{Zr}_4 \text{P}_{6-2x} \text{Si}_{2x} \text{O}_{24} \]
Cyclic Thermal Expansion of BS-25

\[ \text{Ba}_{1+x} \text{Zr}_4\text{P}_{6-2x}\text{Si}_{2x}\text{O}_{24} \]

Atmosphere: Room Air
Heating/Cooling Rate: 3°C/min

- As Sintered
- 1 cycle
- 25 cycles
- 250 cycles

T. Barrett Jackson, LoTEC, Inc.
ORNL-HTML Industrial Fellowship Program
Thermal Conductivity and Diffusivity

Value of $X$ in $\text{Ba}_{1+X}\text{Zr}_4\text{P}_{6-2X}\text{Si}_{2X}\text{O}_{24}$

- Thermal Conductivity
- Thermal Diffusivity

Diagram showing the relationship between the value of $X$ and thermal conductivity and diffusivity.
Thermal Shock Resistance

Value of $x$ in $\text{Ba}_{1+x} \text{Zr}_4 \text{P}_{5.5} \text{Si}_{0.5} \text{O}_{24}$

Thermal Shock Temperature, $^\circ\text{T}$, (°C)
Cyclic Thermal Shock Resistance

Sample size: 10 bars
Composition: \( \text{Ba}_{1.25} \text{Zr}_4 \text{P}_{5.5} \text{Si}_{0.5} \text{O}_{24} \)
Quenched from 1250°C to 2°C water

Four Point Flexural Strength (MPa)

Number of Thermal Shock Cycles
High-Temperature Stability

$\text{Ba}_{1.25}\text{Zr}_4\text{P}_{5.5}\text{Si}_{0.5}\text{O}_{24}$

Initial Specific Surface Area of the sample: 8.5 m$^2$/g
High-Temperature Strength

Sample size: Three samples per temperature

- \( \text{Ba}_{1.25}\text{Zr}_4\text{P}_{5.5}\text{Si}_{0.5}\text{O}_{24} \) (Isotropic CTE)
- \( \text{Ba}_{1.5}\text{Zr}_4\text{P}_5\text{SiO}_{24} \) (Anisotropic CTE)
# Comparison of Low CTE Materials

<table>
<thead>
<tr>
<th>Properties</th>
<th>Units</th>
<th>NZP</th>
<th>Slip Cast fused Silica</th>
<th>Cordierite</th>
<th>Alumum Titanate</th>
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<td><em>Thermal</em></td>
<td></td>
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<td>Thermal Expansion</td>
<td>cm/cm °C C</td>
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<td>5 x 10^{-7}</td>
<td>8 x 10^{-7}</td>
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<td>in/in °F</td>
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<td>5 x 10^{-7}</td>
<td>4 x 10^{-7}</td>
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<td>Thermal Expansion Anisotropy</td>
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<td>50 x 10^{-7}</td>
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<td></td>
<td>in/in °F</td>
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<td>?</td>
<td>28 x 10^{-7}</td>
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<td>Thermal Conductivity</td>
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<td>Btu.in/ft².hr. °F</td>
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<td>Thermal Diffusivity</td>
<td>mm²/s °C</td>
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<td>f²/hr</td>
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<td>Heat Capacity</td>
<td>J/g.°K</td>
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<td>0.6</td>
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<td>Maximum Use Temperature</td>
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<td>Flexural Strength RT</td>
<td>MPa</td>
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<td>Fracture Toughness</td>
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<td>1.5 to 2</td>
<td>1.7</td>
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LoTEC’s Capabilities

- Powder Processing
  - Solid State Oxide Mixing and Calcination & Acid-Base Reaction Chemistry
- Powder Characterization
  - Particle Density, Particle Size Distribution, and Surface Area Analysis
- Bulk Processing and Finishing
  - Uniaxial and Iso-Pressing, Slip casting, Gelcasting, and Injection Molding, Sintering in Air and Atmosphere, and Machining
- Sample Characterization
  - Porosimetry, Dilatometry, Density, Elastic Modulus, Strength & Toughness
- Engineering Design and Analysis
  - Pro-E Solids Modeling and MSC/Nastran Finite Element Analysis
Summary

- Thermophysical properties of [NZP] materials can be tailored by proper ionic substitutions and materials processing techniques.
- Certain [NZP] materials have very low thermal expansion and expansion anisotropy and, in turn, good mechanical properties.
- [NZP] materials exhibit high thermal shock resistance, low thermal conductivity and high melting temperature.
Summary . . .(contd.)

- [NZP] materials can be fabricated using a variety of shape forming processes; components as large as 22" dia. have been fabricated at LoTEC, Inc.
- In addition to solid-state (oxide mixing) synthesis technique, a new technology has been developed for synthesizing [NZP] powders at relatively low cost.
- [NZP] materials are currently in use or being examined for various advanced and traditional ceramic applications.