ENHANCED HIGH TEMPERATURE PIEZOELECTRICS BASED ON BiScO₃-PbTiO₃ CERAMICS

High-temperature piezoelectrics are a key technology for aeronautics and aerospace applications such as fuel modulation to increase the engine efficiency and decrease emissions. The principal challenge for the insertion of piezoelectric materials is the limitation on upper use temperature which is due to low Curie-Temperature (T_C) and increasing electrical conductivity. BiScO₃-PbTiO₃ (BS-PT) system is a promising candidate for improving the operating temperature for piezoelectric actuators due to its high T_C (>400°C). Bi₂O₃ was shown to be a good sintering aid for liquid phase sintering resulting in reduced grain size and increased resistivity. Zr doped and liquid phase sintered BS-PT ceramics exhibited saturated and square hysteresis loops with enhanced remenant polarization (37 µC/cm²) and coercive field (14 kV/cm). BS-PT doped with Mn showed enhanced field induced strain (0.27% at 50kV/cm). All the numbers indicated in parenthesis were collected at 100 °C.
Enhanced High Temperature Piezoelectrics Based on BiScO$_3$-PbTiO$_3$ Ceramics

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Green engines and morphing planes

Active and Passive Vibration Control of Fan Blade Using Piezoceramics

Fuel modulation:
- Increased engine efficiency
- Decreased NO\textsubscript{x} gases

Advantages:
- Fast response time
- Generate large forces
- No gears or rotating shafts, no wear and tear.

Actuators for Aerospace and Aeronautics:
Fuel modulation, valves, micro-positioning devices, MEMS, active damping and energy harvesting.

Sensors:
Pressure sensors, passive damping

• Increased turbine engine operating temperate can dramatically increase fuel efficiency & reduce emissions
• Current DOD study shows only reasonable way to increase engine temperature is by advanced materials
• 2001 Stanford study shows a $1B/year fuel savings if engines run 1 degree C hotter
Challenges for High Temperature Applications

- Trade off between $T_C$ and $d_{33}$
- Conductivity at elevated temperatures

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_{\text{limit}}$ ($^\circ\text{C}$)/($^\circ\text{F}$)</th>
<th>$d_{33}$ (pC/N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZT Type II (PZT 5A)</td>
<td>350 / 662</td>
<td>374</td>
</tr>
<tr>
<td>PMN-PT single crystals</td>
<td>90 / 194</td>
<td>&gt;2000</td>
</tr>
<tr>
<td>BiScO$_3$-PbTiO$_3$</td>
<td>450 / 842</td>
<td>401</td>
</tr>
<tr>
<td>La$<em>3$Ga$</em>{5.5}$Ta$<em>{0.5}$O$</em>{14}$ single crystal</td>
<td>N/A</td>
<td>7</td>
</tr>
<tr>
<td>Na$<em>{0.5}$Bi$</em>{4.5}$Ti$_4$O$_5$</td>
<td>650 / 1202</td>
<td>19</td>
</tr>
<tr>
<td>La$_2$Ti$_2$O$_7$</td>
<td>1482 / 2700</td>
<td>16</td>
</tr>
</tbody>
</table>

Approach and Outline

• Microstructure engineering
  Liquid phase sintering

• Compositional engineering
  – Isovalent doping (Yb, In)
  – Aliovalent doping (Sr, Zr)
  – Multivalent doping (Mn)

• Properties
Processing of BS-PT

- Raw materials (Bi$_2$O$_3$, PbO, Sc$_2$O$_3$, TiO$_2$)
- Ball milling (15hrs)
- Drying (stirred)
- Calcination (750°C, 3hrs, 5°C/min), in air
- Ball milling (6hrs)
- Excess addition
- Pressing
- Sintering (1100°C, 1hr, 5°C/min), in air

Dopants
Sintering conditions

![Graph showing thermal strain over time and temperature](image)

**Thermal strain**

**dL/L₀**

**Temperature (°C)**

**Time (min)**

**dL/L₀ (at 1100 °C)**

**Netzsch horizontal dilatometer**

**5 °C/min, heating, air, alumina push rod**

- **No excess**
- **5% Bi**

- **615 °C**
- **1100 °C**
- **1280 °C**
Effect of Liquid Phase Sintering (via Bi$_2$O$_3$) on microstructure

0% Bi

2% Bi

5% Bi

10% Bi

Bi-oxide

10 microns
Effects of Liquid Phase Sintering in BS-PT

1 kHz, 0.5 V/mm ac, in air
Ferroelectric and piezoelectric properties

Polarization ($\mu$C/cm$^2$)

- No excess
- 5% Bi
- 5% Pb

E-field (kV/cm)

100 °C
Ferroelectric Properties

\[ E_C = 13.5 \text{ kV/cm} \]

5% Bi excess

100 °C

BiScO\textsubscript{3}-PbTiO\textsubscript{3} system
Effects of Zr-doping

Batched composition $0.37\text{Bi(Sc}_{0.98,\text{Zr}_{0.02}}\text{O}_3-0.63\text{PbTiO}_3$

<table>
<thead>
<tr>
<th></th>
<th>Undoped</th>
<th>Doped</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi/(Pb+Bi)</td>
<td>$\approx36$</td>
<td>$\approx36$</td>
</tr>
<tr>
<td>Sc/(Sc+Ti)</td>
<td>$\approx38$</td>
<td>$\approx37.5$</td>
</tr>
<tr>
<td>Volatilization during sintering</td>
<td>91Pb-9Bi</td>
<td>90Pb-10Bi</td>
</tr>
<tr>
<td>Weight loss during sintering (%) by TG</td>
<td>0.17</td>
<td>0.18</td>
</tr>
<tr>
<td>Weight change during sintering (%) (real sample)</td>
<td>- $&lt;2%$</td>
<td>+0.15-0.30</td>
</tr>
<tr>
<td>Grain size ($\mu$m)</td>
<td>$&gt;20$ (bimodal)</td>
<td>$\approx2$</td>
</tr>
</tbody>
</table>

Theoretical: Zr mol% = 0.148

ICP calcined: Zr mol% = 0.144

<table>
<thead>
<tr>
<th></th>
<th>Tetragonal perovskite</th>
<th>Rhombohedral perovskite</th>
<th>Ti Bi$<em>{12}$O$</em>{20}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a$ (Å)</td>
<td>$c$ (Å)</td>
<td>$a$ (Å)</td>
</tr>
<tr>
<td>Zr-doped</td>
<td>3.997</td>
<td>4.052</td>
<td>4.027</td>
</tr>
<tr>
<td>Undoped</td>
<td>3.988</td>
<td>4.055</td>
<td>4.019</td>
</tr>
</tbody>
</table>

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<thead>
<tr>
<th></th>
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<th>Rhombohedral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-doped</td>
<td>0.29</td>
<td>0.71</td>
</tr>
<tr>
<td>Undoped</td>
<td>0.47</td>
<td>0.53</td>
</tr>
</tbody>
</table>

$\text{Zr}_{\text{Sc}} \rightarrow V_{\text{Pb}}^{\perp\perp}, V_{\text{Bi}}^{\perp\perp}, O_{V}^{\perp\perp}, \text{Pb}_{\text{Bi}}^{\perp\perp}$
Doping comparison

<table>
<thead>
<tr>
<th></th>
<th>Nominal</th>
<th>5% Bi</th>
<th>Zr-doping</th>
<th>PZT II</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d\varepsilon_{max}/dE_{max}$ (pm/V)</td>
<td>354</td>
<td>408</td>
<td>500</td>
<td>585</td>
</tr>
</tbody>
</table>
Doping comparison (2)

<table>
<thead>
<tr>
<th></th>
<th>Nominal</th>
<th>5% Bi</th>
<th>Zr-doping</th>
<th>PZT II</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_r$ ($\mu$C/cm²)</td>
<td>46.4</td>
<td>36.6</td>
<td>43</td>
<td>36.4</td>
</tr>
<tr>
<td>$E_C$ (kV/cm)</td>
<td>19</td>
<td>13.3</td>
<td>11.8</td>
<td>9.25</td>
</tr>
</tbody>
</table>
Doping comparison (3)

E_c for PZT at 20°C = E_c for Zr-doped at 100°C

Next step is to increase k_p
Effect of liquid phase sintering

Micro-structural Engineering: Liquid phase sintering

$\text{Bi}_2\text{O}_3$ is added as a liquid phase sintering aid

- Faster densification
- Smaller grain size
- Non-continuous grain boundary phase

Improved dielectric loss at elevated temperatures
High Curie Temperature remain unchanged

<table>
<thead>
<tr>
<th></th>
<th>LPS $\text{BiScO}_3$-$\text{PbTiO}_3$</th>
<th>PZT-Type II</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_C$ (°C)</td>
<td>430</td>
<td>315</td>
</tr>
<tr>
<td>$d_{33}$ (pC/N)</td>
<td>408</td>
<td>585</td>
</tr>
<tr>
<td>$E_C$ (kV/cm)</td>
<td>13</td>
<td>9</td>
</tr>
<tr>
<td>$P_R$ ($\mu$C/cm$^2$)</td>
<td>37</td>
<td>36</td>
</tr>
<tr>
<td>$\rho_{DC}$ ($\Omega$.cm)</td>
<td>$\approx 10^{11}$</td>
<td>$\approx 10^{11}$</td>
</tr>
</tbody>
</table>


High field $d_{33}$ is an approximation of max induced strain / max field at 100 °C.
Effect of compositional modification

Compositional Engineering: Donor doping

Zr\(^4+\) is added as a donor in place of Sc\(^3+\)

0.37Bi(Sc\(_{0.98}Zr\(_{0.02}\))O_3 - 0.63PbTiO_3

<table>
<thead>
<tr>
<th></th>
<th>Zr-doped BS-PT</th>
<th>LPS BS-PT</th>
<th>PZT Type II</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_C) (°C)</td>
<td>404</td>
<td>430</td>
<td>315</td>
</tr>
<tr>
<td>(d_{33}) (pC/N)</td>
<td>500</td>
<td>408</td>
<td>585</td>
</tr>
<tr>
<td>(E_C) (kV/cm)</td>
<td>21</td>
<td>23</td>
<td>12</td>
</tr>
<tr>
<td>(P_R) ((\mu)C/cm(^2))</td>
<td>43</td>
<td>24</td>
<td>44</td>
</tr>
<tr>
<td>(\rho_{DC}) (Ωcm)</td>
<td>(\approx 10^{11})</td>
<td>(\approx 10^{11})</td>
<td>(\approx 10^{11})</td>
</tr>
</tbody>
</table>

High field \(d_{33}\) is an approximation of max induced strain / max field

Improved operating temperature
Improved coercive field
Improved remanent polarization
Acknowledgements

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