ENHANCED HIGH TEMPERATURE PIEZOELECTRICS BASED ON BiScO$_3$-PbTiO$_3$ 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. BiScO$_3$-PbTiO$_3$ (BS-PT) system is a promising candidate for improving the operating temperature for piezoelectric actuators due to its high $T_C$ (>400°C). Bi$_2$O$_3$ 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 $\mu$C/cm$^2$) 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 BiScO₃-PbTiO₃ 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$_x$ 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
Challenges for High Temperature Applications

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

<table>
<thead>
<tr>
<th></th>
<th>$T_{\text{limit}}$ (°C)/(°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

Dopants

Sintering (1100°C, 1hr, 5°C/min), in air

![X-ray diffraction pattern with peaks at 2θ values: (001), (002), (110), (111), (201), (210), (211), (220), (212), (301).]
Sintering conditions

Thermal strain $\frac{dL}{L_0}$ vs. Temperature ($^\circ$C)

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

Netzsch horizontal dilatometer
5 °C/min, heating, air, alumina push rod

Key temperatures:
- 615 °C
- 1280 °C
- 1100 °C

Time (min)
0 10 20 30 40 50 60 70

$\frac{dL}{L_0}$ (at 1100 °C)
0.00 0.02 0.04 0.06 0.08 0.10
Effect of Liquid Phase Sintering (via Bi$_2$O$_3$) on microstructure
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

No excess

$E_C = 13.5 \text{ kV/cm}$

5% Bi excess
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 (µm) (bimodal)</td>
<td>&gt;20</td>
<td>(\approx2)</td>
</tr>
</tbody>
</table>

Relative ratio: Tetragonal: Rhombohedral

<table>
<thead>
<tr>
<th></th>
<th>Tetragonal</th>
<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>

Zr\text{Sc} \rightarrow V_{\text{Pb}^{\parallel}} , V_{\text{Bi}^{\parallel\parallel}} , O_{\text{V}^{\parallel\parallel}} , Pb_{\text{Bi}^{\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>$d_{\varepsilon_{\text{max}}}/dE_{\text{max}}$ (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>$P_r$ (µC/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>

100 °C

DC-resistivity (Ω.cm)

Polarization (µC/cm²)

- No excess
- 5% Bi
- Zr-doping
- PZT II
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

Bi₂O₃ 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 BiScO₃-PbTiO₃</th>
<th>PZT-Type II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tc (°C)</td>
<td>430</td>
<td>315</td>
</tr>
<tr>
<td>d₃₃ (pC/N)</td>
<td>408</td>
<td>585</td>
</tr>
<tr>
<td>Ec (kV/cm)</td>
<td>13</td>
<td>9</td>
</tr>
<tr>
<td>Pr (μC/cm²)</td>
<td>37</td>
<td>36</td>
</tr>
<tr>
<td>ρDC (Ω.cm)</td>
<td>≈ 10^{11}</td>
<td>≈ 10^{11}</td>
</tr>
</tbody>
</table>

High field d₃₃ 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$^{3+}$

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

<table>
<thead>
<tr>
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<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>$\rho_{DC}$ ($\Omega$.cm)</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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