Doping of BiScO$_3$-PbTiO$_3$ Ceramics for Enhanced Properties

Alp Sehirlioglu$^1$, Ali Sayir$^{1,2}$ and Fred Dynys$^2$
1 Case Western Reserve University, Cleveland, OH
2 NASA Glenn Research Center, Cleveland, OH

Abstract
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$^\circ$C). Effects of Zr and Mn doping of the BS-PT ceramics have been studied and all electrical and electromechanical properties for Sc-deficient and Ti-deficient BS-PT ceramics are reported as a function of electrical field and temperature. Donor doping with Zr and Mn (in Sc deficient compositions) increased the DC-resistivity and decreased tan$\delta$ at all temperatures. Resulting ceramics exhibited saturated hysteresis loops with low losses and showed no dependence on the applied field (above twice the coercive field) and measurement frequency.
Doping of BiScO$_3$-PbTiO$_3$ ceramics for enhanced properties

Alp Sehirlioglu$^1$, Ali Sayir$^{1,2}$ and Fred Dynys$^2$

$^1$ Case Western Reserve University, Cleveland, OH
$^2$ NASA Glenn Research Center, Cleveland, OH

AFOSR FA 9550-06-1-0260
Objective

Development of high-temperature piezoelectric actuators for aeronautics and aerospace applications.

Applications

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

• Sensors
  – Pressure sensors, passive damping

Advantages

• Fast response time
• Generate large forces
• No gears or rotating shafts, no wear and tear.
Challenges for High Temperature

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

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

• Microstructure engineering
  Liquid phase sintering

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

Liquid phase sintering

Effects of excess Pb and Bi

Electromechanical properties

Compositional modifications
Processing of BS-PT

Raw materials (Bi₂O₃, PbO, Sc₂O₃, TiO₂)

Dopants

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
Effect of Bi on microstructure

0% Bi

2% Bi

5% Bi

10% Bi

Bi-oxide
Effects of Bi in BS-PT

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

Polarization (μC/cm²)

No excess
5% Bi
5% Pb

E-field (kV/cm)

100 °C
Ferroelectric Properties

No excess

100 °C

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

5% Bi excess

100 °C

BiScO$_3$-PbTiO$_3$ system
Unipolar frequency dependence

No excess

5% Bi excess

100 °C
Unipolar polarization

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

- Black line: No excess
- Red line: 5% Bi excess

100 °C

5% Bi

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

- Black line: 30 C
- Red line: 100 C
- Blue line: 180 C

E-field (kV/cm)
Piezoelectric coefficient

\[ d_{33} = 408 \text{ pC/N} \]

\[ d_{33} = 354 \text{ pC/N} \]

5% Bi excess

No excess

100 °C

E-field (kV/cm)

Strain (%)

E-field (kV/cm)

Strain (%)

30 °C

100 °C

180 °C
High field resistivity

100 °C

5% Bi
Doping comparison

<table>
<thead>
<tr>
<th></th>
<th>Nominal</th>
<th>5% Bi</th>
<th>Zr-doping</th>
<th>Mn-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>542</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>Mn-doping</th>
<th>PZT II</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_r$ ($\mu$C/cm$^2$)</td>
<td>46.4</td>
<td>36.6</td>
<td>43</td>
<td>21.3</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>11.2</td>
<td>9.25</td>
</tr>
</tbody>
</table>
Doping comparison (3)

\[ \varepsilon'' = \varepsilon' \times \tan \delta \]

\( \varepsilon' = \) Dielectric constant
\( \varepsilon'' = \) Dielectric loss
\( \tan \delta = \) Loss tangent

<table>
<thead>
<tr>
<th></th>
<th>5% Bi</th>
<th>Mn-doping</th>
<th>PZT II</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_C ) (°C)</td>
<td>432</td>
<td>414</td>
<td>316</td>
</tr>
</tbody>
</table>
Materials for high temperature actuators

**FA 9550-06-1-0260**

**MAIN ACHIEVEMENT:**
Piezoelectric activity in the level of state of the art materials have been achieved.

**HOW IT WORKS:**
BiScO$_3$-PbTiO$_3$ ceramics have been improved by concurrent engineering of:
- **Microstructure:** Optimized microstructure via liquid phase sintering\(^1\) and decreased the high field and high temperature losses.\(^2\)
- **Composition:** Modified the composition by isovalent and aliovalent doping to increase the electromechanical properties.

**ASSUMPTIONS AND LIMITATIONS:**
- Needs further optimization through combination of the two approaches and multi-doping strategies.
- The developed material needs to be demonstrated as a part of an actuator

\(^1\) Journal of the American Ceramic Society, accepted
\(^2\) Journal of Applied Physics, submitted

High temperature piezoelectrics enable active combustion control in jet engines that can increase engine efficiency and reduce emissions