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°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.
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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 (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
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 vs. E-field graph](image)

- **Polarization** ($\mu$C/cm$^2$)
- **E-field** (kV/cm)
- **100 °C**

Graph shows the polarization behavior under different E-fields for samples with and without excess and with 5% Bi and 5% Pb.
Ferroelectric Properties

No excess

BiScO$_3$-PbTiO$_3$ system

$E_C = 13.5$ kV/cm

100 °C

5% Bi excess
Unipolar frequency dependence

100 °C

No excess

5% Bi excess

100 °C

Polarization (μC/cm²)

E-field (kV/cm)

1 sec w/ 5%Bi

13 sec

9 sec

5 sec

1 sec
Unipolar polarization

5% Bi

100 °C
Piezoelectric coefficient

- 5% Bi excess: $d_{33} = 408 \text{ pC/N}$
- No excess: $d_{33} = 354 \text{ pC/N}$

- 100 °C
High field resistivity

DC-Resistivity (Ω·cm)

Electric Field (kV/cm)

5% Bi

100 °C

Resistivity (Ω·cm)

Electric Field (kV/cm)

- No excess
- 5% Bi

- 30 °C
- 100 °C
- 180 °C
Doping comparison

### Table: $d\varepsilon_{\text{max}}/dE_{\text{max}}$ (pm/V)

<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>

PZT II by Piezo Kinetics, Inc
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)

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

\[ \varepsilon' = \text{Dielectric constant} \]

\[ \varepsilon'' = \text{Dielectric loss} \]

\[ \tan \delta = \text{Loss tangent} \]

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

**Status Quo**

Now mature PZT system is limited up to 180°C for the upper use temperature
- Higher Curie Temperature is needed
- Lower conductivity at elevated temperatures is required

**New Insights**

BiScO₃-PbTiO₃ (BS-PT) has high Curie temperature and large piezoelectric coefficients
It is promising to be operational at higher temperatures than PZT via microstructural and compositional refining

**Main Achievement:**
Piezoelectric activity in the level of state of the art materials have been achieved.

**How it works:**
BiScO₃-PbTiO₃ ceramics have been improved by concurrent engineering of:
- **Microstructure:** Optimized microstructure via liquid phase sintering¹ and decreased the high field and high temperature losses.²
- **Composition:** Modified the composition by isovalent and aliovalent doping to increase the electro-mechanical 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

**End-of-phase goal**
Build piezoelectric stack-actuators for high temperature applications
- Optimize the composition and microstructure
- Develop necessary electrodes, leads and encapsulation material

**Quantitative Impact**

End-of-phase goal
- 200 °C $d_{33} = 200 \text{ pC/N}$
- 300 °C $d_{33} = 200 \text{ pC/N}$

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