Effect of excess lead and bismuth content on the electrical properties of high-temperature bismuth scandium lead titanate ceramics

Alp Sehirlioglu and Ali Sayir
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Aeronautic and aerospace applications require piezoelectric materials that can operate at high temperatures. The air-breathing aeronautic engines can use piezoelectric actuators for active combustion control for fuel modulation to mitigate thermo-acoustic instabilities and/or gas flow control to improve efficiency. The principal challenge for the insertion of piezoelectric materials is their limitation for upper use temperature and this limitation is due low Curie temperature and increasing conductivity. We investigated processing, microstructure and property relationship of (1-x)BiScO$_3$-(x)PbTiO$_3$ (BS-PT) composition as a promising high temperature piezoelectric. The effect of excess Pb and Bi and their partitioning in grain boundaries were studied using impedance spectroscopy, ferroelectric, and piezoelectric measurement techniques. Excess Pb addition increased the grain boundary conduction and the grain boundary area (average grain size was 24.8\textmu m, and 1.3\textmu m for compositions with 0at.% and 5at.% excess Pb, respectively) resulting in ceramics with higher AC conductivity (tan $\delta$= 0.9 and 1.7 for 0at.% and 5at.% excess Pb at 350 $^\circ$C and at 10kHz) that were not resistive enough to pole. Excess Bi addition increased the resistivity ($\rho$= 4.1x10$^{10}$ $\Omega$.cm and 19.6 x10$^{10}$ $\Omega$.cm for compositions with 0at.% and 5at.% excess Bi, respectively), improved poling, and increased the piezoelectric coefficient from 137 to 197 pC/N for 5at.% excess Bi addition. In addition, loss tangent decreased more than one order of magnitude at elevated temperatures (>300 $^\circ$C). For all compositions the activation energy of the conducting species was similar ($\approx$ 0.35-0.40 eV) and indicated electronic conduction.
Effect of excess PbO and Bi$_2$O$_3$ content on the electrical properties of high-temperature BiScO$_3$-PbTiO$_3$ ceramics

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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
Challenges for High Temperature

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

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_{lim}$ (°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>$La_3Ga_{5.5}Ta_{0.5}O_{14}$ single crystal</td>
<td>N/A</td>
<td>7</td>
</tr>
<tr>
<td>Na$<em>{0.5}$Bi$</em>{4.5}$Ti$<em>4$O$</em>{15}$</td>
<td>650 / 1202</td>
<td>19</td>
</tr>
<tr>
<td>La$_2$Ti$_4$O$_7$</td>
<td>1482 / 2700</td>
<td>16</td>
</tr>
</tbody>
</table>


Processing of BS-PT

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

- Impedance measurements (Solartron and HP Agilent)
  - 1Hz-1MHz, Room temperature to 1000 °C.
  - 40Hz-110MHz, Room temperature to 600 °C.
  - 1Mhz-3Ghz, Microwave range
    (Determination of electrical, dielectric and electromechanical properties)

- Ferroelectric measurements (Radiant Technologies)
  - Bipolar, unipolar loops, leakage (up to 10,000V)

- Piezoelectric measurements
  - Laser dopplermeter (Polytech) coupled with a signal generator and a high power amplifier (up to 10,000V)
  - PhotonicTM sensor (MTI technologies) coupled with Radiant
  - Berlincourt $d_{33}$ -meter

Effect of Pb on microstructure
Effect of Pb in BS-PT

10 kHz, 0.5 V/mm ac, in air

<table>
<thead>
<tr>
<th>Pb Content</th>
<th>Relaxation Frequency</th>
<th>5 kHz</th>
<th>3 kHz</th>
<th>800 Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% Pb</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2% Pb</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5% Pb</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Dielectric constant

<table>
<thead>
<tr>
<th>Pb Content</th>
<th>Relaxation Frequency</th>
<th>5 kHz</th>
<th>3 kHz</th>
<th>800 Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% Pb</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2% Pb</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5% Pb</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Grain boundary contribution

<table>
<thead>
<tr>
<th>Pb Content</th>
<th>ε_{ac} (ev)</th>
<th>ρ_{grain} (Ω.cm)</th>
<th>K_{grain}</th>
<th>E_{ac} (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% Pb</td>
<td></td>
<td>4.1x10^{10}</td>
<td>1085</td>
<td>0.36</td>
</tr>
<tr>
<td>2% Pb</td>
<td></td>
<td>2.4x10^{10}</td>
<td>805</td>
<td>0.35</td>
</tr>
<tr>
<td>5% Pb</td>
<td></td>
<td>1.4x10^{10}</td>
<td>727</td>
<td>0.35</td>
</tr>
</tbody>
</table>
Effect of Bi on microstructure

Effects of Bi in BS-PT

1 kHz, 0.5 V/mm ac, in air
Effect of Bi in BS-PT

<table>
<thead>
<tr>
<th></th>
<th>$\rho_{\text{grain}}$ (Ω.cm)</th>
<th>Dielectric constant, $K_{\text{grain}}$</th>
<th>Relaxation freq.</th>
<th>$E_{\text{ac}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No excess</td>
<td>$4.1 \times 10^{10}$</td>
<td>1085</td>
<td>800 Hz</td>
<td>0.36</td>
</tr>
<tr>
<td>2% Bi</td>
<td>$4.9 \times 10^{10}$</td>
<td>1104</td>
<td>400 Hz</td>
<td>0.40</td>
</tr>
<tr>
<td>5% Bi</td>
<td>$19.6 \times 10^{10}$</td>
<td>1402</td>
<td>200 Hz</td>
<td>0.20, 0.59</td>
</tr>
</tbody>
</table>

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

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

100 °C

5% Bi excess

Unipolar frequency dependence

5% Bi excess

100 °C

No excess

100 °C
Piezoelectric coefficient

Strain (%)

- 5% Bi excess
- No excess

$\varepsilon_{33} = 408 \text{ pC/N}$

$\varepsilon_{33} = 354 \text{ pC/N}$

E-field (kV/cm)

High field resistivity

Resistivity (Ω.cm)

- No excess
- 5% Bi

100 °C

Electric Field (kV/cm)
Summary

- BiScO$_3$-PbTiO$_3$ ceramics with $T_C > 400^\circ$C has been successfully processed.
- Despite the increase in $T_C$, excess Pb addition increases both the bulk conductivity and the grain boundary contribution to conductivity at elevated temperatures.
- Conductivity at elevated temperatures, that limits the operating temperature for actuators, has been greatly reduced by excess Bi additions.
- Excess Bi doping improves poling conditions resulting in enhanced piezoelectric coefficient ($d_{33} = 408$ pC/N).

![Resonance frequencies graph](image)

- Fundamental frequency (Hz)
- Overtone frequency (Hz)
- Temperature (°C)
Resonance frequencies

ICP

<table>
<thead>
<tr>
<th></th>
<th>Bi/ (Bi+Pb)</th>
<th>Pb/ (Bi+Pb)</th>
<th>Sc/ (Sc+Ti)</th>
<th>Ti/ (Sc+Ti)</th>
<th>O/ (Bi+Pb)</th>
<th>O/ (Sc+Ti)</th>
<th>O[^{\text{II}}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcined</td>
<td>0.372</td>
<td>0.628</td>
<td>0.358</td>
<td>0.642</td>
<td>2.515</td>
<td>2.411</td>
<td>2.865</td>
</tr>
<tr>
<td>Sintered</td>
<td>0.369</td>
<td>0.631</td>
<td>0.360</td>
<td>0.640</td>
<td>2.624</td>
<td>2.563</td>
<td>2.845</td>
</tr>
</tbody>
</table>

\[^{\text{II}}\] Last column shows oxygen measured by the Oxygen Determinator. Three repeats were done on each powder sample. Due to the high oxygen content the sample size taken was around 5mg. The accuracy was estimated to be ± 0.25wt%. 
Impedance calculations

<table>
<thead>
<tr>
<th>Composition</th>
<th>Grain size (µm)</th>
<th>$\rho_{\text{grain}}$ (Ω.cm) at 55 ºC</th>
<th>$K_{\text{grain}}$ at 55 ºC</th>
<th>Relax.freq. (Hz) at 325 ºC</th>
<th>$E_{\text{ac}}$ (eV) from $\rho$</th>
<th>$E_{\text{ac}}$ (eV) from $\tau$</th>
</tr>
</thead>
<tbody>
<tr>
<td>No excess</td>
<td>24.8</td>
<td>4.1 x 10^10</td>
<td>1085</td>
<td>800</td>
<td>0.36</td>
<td>0.36</td>
</tr>
<tr>
<td>2% Pb</td>
<td>5.6</td>
<td>2.4 x 10^10</td>
<td>805</td>
<td>3000</td>
<td>0.35</td>
<td>0.32</td>
</tr>
<tr>
<td>5% Pb</td>
<td>1.3</td>
<td>1.4 x 10^10</td>
<td>727</td>
<td>5000</td>
<td>0.35</td>
<td>0.33</td>
</tr>
<tr>
<td>2% Bi</td>
<td>18.6</td>
<td>4.9 x 10^10</td>
<td>1104</td>
<td>400</td>
<td>0.40</td>
<td>0.40</td>
</tr>
<tr>
<td>5% Bi</td>
<td>3.35</td>
<td>19.6 x 10^10</td>
<td>1402</td>
<td>40</td>
<td>0.20</td>
<td>0.59</td>
</tr>
</tbody>
</table>

Sintering Conditions for BS-PT

Netzch horizontal dilatometer
5ºC/min, heating, air, alumina push rod

1200 ºC
1100 ºC
615 ºC
1280 ºC

Temperature (ºC)

$E_{\text{ac}}$ (eV) from $\tau$
Impedance Spectroscopy

Conductivity - Grain/Grain Boundary

\[ \omega_0 = \frac{1}{RC} \]

- \( \omega_{\text{max}} \)
- \( \omega_{\text{min}} \)

Real Impedance (Ω) - Imaginary Impedance (Ω)

Grain Interior Grain Boundary Electrodes

R // C : Resonance frequency \( \omega_0 = 1/RC \)

Conduction: grain ≠ grain boundary

\( \omega_0 \) grain boundary << \( \omega_0 \) grain-Low T

\( \omega_0 \) grain boundary ~ \( \omega_0 \) grain-High T