Effects of dopant on depoling temperature in modified BiScO$_3$ – PbTiO$_3$

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Introduction

• Piezoelectrics for high temperature applications
  – Fuel/gas modulation, ultrasonic drilling, etc.
• Tolerance factor \((t)\) acts as guide for selection of non-PT member
• BiScO\(_3\) – PbTiO\(_3\):
  – \(T_c: 450^{\circ}C\), \(d_{33}: 460\ \text{pm/V}\) for morphotropic phase boundary (MPB) composition

– A-site modification: La, Ba
– B-site modification: Ga, Mn, Zr, Zn\(_{0.5}\)Ti\(_{0.5}\), Nb, etc.
– DC conductivity, \(\tan\delta\), \(d_{33}\), \(T_c\), \(T_d\), etc.


Dopant effects on depoling temperature in BS-PT
A different metric

- Curie temperature ($T_c$) doesn’t tell whole story
- Many piezoelectric materials depole before $T_c$
- Why do they depole? Domain rotation, phase transitions, inhomogeneities
- Dope to change depoling temperature

Compositions

- Previous success with aliovalent Zr$_{Sc}$ and compensated Zn$_{0.5}$Zr$_{0.5}$ on Sc
  - 2% Zr$_{Sc}$ increases $T_d$ by 20°C for 37BS – 63PT, with a decrease in $T_c$
- Compositions chosen from rhombohedral and tetragonal regions around MPB
- Aliovalent Zn$_{Sc}$ chosen for high ferroelectric activity; hybridizes similarly to Ti
- Conventional solid state processing
  - Calcine: 3hrs @ 750°C
  - Sinter: 1hr @ 1100°C

Nomenclature

<table>
<thead>
<tr>
<th>Zn Concentration</th>
<th>BSPT58</th>
<th>BSPT60</th>
<th>BSPT62</th>
<th>BSPT64</th>
<th>BSPT66</th>
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<tr>
<td>0% Zn</td>
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<tr>
<td>1% Zn</td>
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<td>--</td>
<td>BSPT621</td>
<td>BSPT641</td>
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<tr>
<td>2% Zn</td>
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<td>BSPT622</td>
<td>BSPT642</td>
<td>BSPT625</td>
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<td>5% Zn</td>
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<td>--</td>
<td>BSPT625</td>
<td>BSPT645</td>
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Zr$_{Sc}$ doping – Sehirlioglu et al, J. Am. Cer. Soc., 2010
Zn$_{0.5}$Zr$_{0.5}$ doping – Kowalski et al, J. Am. Cer. Soc., 2013
X-ray Diffraction Comparison

- BSPT62: Shifting rhombohedral/tetragonal ratio
- BSPT64: Increasing c/a ratio (1.011 to 1.013) with Zn addition
- ★: Pb$_x$Bi$_{(1-x)}$O phase
Optical Microscopy

- Density: > 96%; dense structures with low porosity
- Grain Size: tends to increase with Zn addition
- Size distribution: possible promotion of abnormal grain growth with Zn addition
- Pb$_x$Bi$_{(1-x)}$O observed in clusters at grain boundaries
### Weak Field Measurements

#### 1kHz

<table>
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<tr>
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<tbody>
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<td>$\varepsilon_r$, 50°C</td>
<td>550</td>
<td>659</td>
<td>633</td>
<td>865</td>
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<td>$\varepsilon_r$, 300°C</td>
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<td>1686</td>
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<td>tanδ 50°C</td>
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<td>0.007</td>
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<td>tanδ 300°C</td>
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#### 100kHz

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<td>836</td>
<td>675</td>
<td>643</td>
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<td>$\varepsilon_r$, 300°C</td>
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<td>0.007</td>
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<td>tanδ 300°C</td>
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<td>0.782</td>
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<td>0.952</td>
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<tr>
<td>$\varepsilon''$, 50°C</td>
<td>12.14</td>
<td>5.02</td>
<td>4.73</td>
<td>3.22</td>
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<tr>
<td>$\varepsilon''$, 300°C</td>
<td>1888</td>
<td>2402</td>
<td>2267</td>
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Weak Field Measurements

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$\phi$ and $\tan\phi$ values at 50°C and 300°C for different dopant concentrations.
High Field Measurements

- Poled at 100°C under 40kV/cm for 30 min.
- BSPT62: Increased $E_c$, $P_r$ with Zn addition
- Assymetric hysteresis
  - Doesn’t fully depole upon switching; Possible pinning from defects
Phase angle (θ) – BSPT58

- Phase angle: 100Hz to 3MHz
- Width in phase angle peak related to coupling coefficients
Phase angle (θ) – BSPT58

- Phase angle: 100Hz to 3MHz
- Width in phase angle peak related to coupling coefficients
Phase angle (θ) – BSPT

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Phase angle (θ) – BSPT
Phase angle ($\theta$) - Transitions

Temperature ($T$) vs. frequency ($F_{\text{freq}}$) graphs for different samples (BSPT58, BSPT60, BSPT62, BSPT64, BSPT66) showing the transition temperatures ($T_c$, $T_{d_{\text{onset}}}$, $T_{d_{\text{final}}}$). The graphs display the temperature at which different frequencies ($F_{\text{freq}}$) are observed, with color intensity indicating the magnitude of the signal. The insets show the 200 peaks at different frequencies for each sample, indicating the phase transition behavior.
Phase angle ($\theta$) - Transitions

Phase angle ($\theta$) - Comparison

Dopant effects on depoling temperature in BS-PT
Phase angle ($\theta$) - Transitions

Dopant effects on depoling temperature in BS-PT
**Zn\textsubscript{0.5}Zr\textsubscript{0.5} for Sc**

- **BZZ2**: $60\text{PbTiO}_3 - 40\text{Bi}[0.9375\text{Sc},0.0625(\text{Zn}_{0.5}\text{Zr}_{0.5})]\text{O}_3$
- **BZZ5**: $62.5\text{PbTiO}_3 - 37.5\text{Bi}[0.933\text{Sc},0.066(\text{Zn}_{0.5}\text{Zr}_{0.5})]\text{O}_3$

Zn\textsubscript{0.5}Zr\textsubscript{0.5} doping – Kowalski et al, J. Am. Cer. Soc., 2013
Zn$_{0.5}$Zr$_{0.5}$ for Sc

- **BZZ2**: $60\text{PbTiO}_3 - 40\text{Bi}[0.9375\text{Sc},0.0625(Zn_{0.5}Zr_{0.5})]O_3$
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Zn$_{0.5}$Zr$_{0.5}$ doping – Kowalski et al, J. Am. Cer. Soc., 2013
Conclusions

• We looked at the effects of Zn$_{Sc}$ on $T_d$ and relevant properties
• Zn$_{Sc}$ increases $T_{d,\text{onset}}$ for BSPT62 compositions while also slightly enhancing electromechanical properties
• Structure specific tan$\delta$ behavior for Zn$_{Sc}$
• Zn$_{0.5}Zr_{0.5}$ increases electromechanical properties and $T_{d,\text{onset}}$
• Combine with other aliovalent dopants to tailor properties further
Would like to thank:
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