High Temperature Ferroelectrics for Actuators: Recent Developments and Challenges

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Venus

- Development of Earth-like planets in our solar system and elsewhere.
- Pathways toward habitable environments.
- Determine planet evolution: The nature, geochemical composition, surface and atmosphere interaction and the role of impacting objects.
- Venus is a planet very similar to Earth in mass, size and bulk density, but very different in surface environment and general geology.
- The Venera and Vega lander missions were accomplishments, but their chemical analyses did not permit detailed confident interpretation by the standards of terrestrial rock analyses.
- The harsh Venus environment caused short mission durations under two hours.

Surface Temperature:
467 °C
Hotter than Mercury due to atmosphere
96.5% carbon dioxide (CO₂)
3.5% nitrogen (N₂)
Surface Pressure
92 bars
High radiation and chemical/physical corrosion
Ultrasonic drilling

- Future NASA missions, New Frontier (Venus In-Situ Surface Explorer) and Flagship (e.g., Venus Surface Explorer and Venus Sample Return), will require advanced surface drilling technology to extract cores from the subsurface.
- Ultrasonic drills driven by piezoelectric motors offer significant advantages over rotary electric motors in terms weight, volume, and power requirement.
- Technology developed by Jet Propulsion Laboratory and Cybersonics.


The ultrasonic drill design is compact, low mass of 450 grams and low power consumption of 5W. Presently, ultrasonic drill technology does not exist for harsh environments due to low operational temperature of the piezoelectric materials. Piezoelectric actuators are smaller, lighter, cheaper and outperform magnetostrictive actuators at high frequencies.
Motivation

- Stirling heat engine technology to replace RTG.
- Increase conversion efficiency, reduce launch mass (specific power > 10 W/kg) and reduce cost.
- Reduces the Pu238 mass for safety cost.
- Several technical challenges: vibrations, electromagnetic interference and reliability/life due to piston motion.

- Piezoelectric technology eliminates electromagnetic interference, enhances reliability/life by eliminating motion, reduces vibration caused by piston motion and reduces mass by eliminating magnets and coils required for power generation.
- Stirling engines have conversion efficiency on the order of 20-30%, linear alternators operate with >90% efficiency.
- Achieve 10-100 watt generator using piezoelectric technology.

- Nine proposed missions to the surface of Venus launching between 2016-2040.
- No other technology capable of supporting long-lived surface operations.
Challenges

Piezoelectric Coefficient vs. Curie Temperature

Loss Tangent and ac Conductivity

High Field Properties and Leakage

Depoling Temperature vs. Curie Temperature


Thermal Depoling Temperature

Thermally activated randomization of domains in ferroelectrics resulting in decreasing net polarization and piezoelectricity with or without a FE-FE or $T>T_f$ phase transformation. Weakening of bonds between A-site cations and oxygen atoms.

**How to define depolarization:** E.M. Anton, W. Jo, D. Damjanovic, and J. Rödel, J.Appl.Phys. 110, 094108 (2011)

$$T_d = \text{the temperature of the steepest decrease of remanent polarization.}$$

1- Thermally stimulated depolarization current
2- Dielectric constant / tan $\delta$ characteristics as a function of temperature
3- Resonance peaks and electromechanical coupling coefficients.
4- Annealing and room temperature $d_{33}$
5- In-situ XRD
6- In situ temperature-dependent piezoelectric coefficient $d_{33}$

Piezoelectric Ceramics


H.C. Materials Corp.


- Tri→M→PC→R→T
- Hybridization of Bi-6p and O-2p orbitals drive the FE instabilities.
- Strong Bi- O covalency favoring FE and high Tc.
- Competition between presence of Bi and decreasing t for FE activity, and random field effects

Tri→M→PC→R→T

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• A-site distortion magnitude depends on the B-site cation
• In T phase – larger cations forming (001) face, (i) smaller displacement, (ii) tilt in the distortion direction.
• Larger B cations will shift the $x$(MPB) to higher PT content

\[ T_c(x) = a + bx + cx^2 \]

- case 1: $b > 0$ and $c > 0$,
- case 2: $b > 0$, $c < 0$, and $|2c| > b$,
- case 3: $b < 0$ and $c < 0$,

• Additional requirement for t-Tc trend: Enhancement of $T_c$ in tetragonal phase (Case II)
• Spread of tolerance factor $\Delta t$: Difference between max and min permissible $t$ in a solid solution.
• Variance of B-site ionic radius ($\sigma^2$).
• Effectively, the largest $\Delta t$ and $\sigma^2$ values give the greatest enhancement in transition temperature.
• Random strain fields

**High $T_c$ with high tetragonality = problem**

xBiFeO$_3$-(1-x)PbTiO$_3$: R3c, $T_c$ = 836$^\circ$C,
- MPB: $x$ = 0.66-0.73
- $c/a$ near MPB: 1.187 (1.06 for PT)
- Possible intermediate phase at MPB
- Fragile: large $c/a$ and NTEC

Properties:
- Highly conductive
- Difficult to pole both due to tetragonality and conductivity (ferroelastic measurements show unstable domains)
- Thermal hysteresis
- Adding BaTiO$_3$ improves resistivity at the cost of $T_c$ but the dielectric losses remain high.
- Attempts to decrease conductivity, decreased $T_c$

Stein, Suchomel, and Davies Appl. Phys. Lett. 89, 132907 2006

xBi(Zn,Ti)O$_3$-(1-x)PbTiO$_3$ → similar problems to BF-PT. Zn, Ti, and Fe are all FE-active, stronger coupling between A- and B-site distortions.

vs. xBi(Mg,Ti)O$_3$-(1-x)PbTiO$_3$: Mg$^{2+}$:72pm, Zn$^{2+}$:74pm → importance of off-centering
MPB $x$ = 0.37, higher $T_c$ than BS, lower $d_{33}$

vs. xBi(Zn,Zr)O$_3$-(1-x)PbTiO$_3$: Zr$^{4+}$:72pm, Ti$^{2+}$:60.5pm → limited displacement of Zr
limited solubility, MPB cannot be processed.

Case II materials

- Necessary to get high $T_c$ at the MPB
- $x\text{Bi}(\text{Mg,Ti})\text{O}_3-(1-x)\text{PbTiO}_3$ $T_c>400^\circ\text{C}$, $d_{33}>200\text{pm/V}$
  - R3c-P4mm core shell structure at MPB with R core and T shell, with frozen in polarization state (no frequency dispersion).
  - Poling can change the local symmetry
- $x\text{Bi}(\text{Ni,Ti})\text{O}_3-(1-x)\text{PbTiO}_3$
  - High conductivity and dielectric losses
- BMT metastable, high pressure synthesis, O, AFE, with strong driving force for ordering
- At 325$^\circ\text{C}$ pseudo-cubic peak appears – so there might be a phase coexistence range (similar to BF-PT, BS-PT)
  - Chen et al., Journal of Applied Physics 106, 034109 (2009)
- $T_d$ lower for $d_{33}$ than tan $\delta$, $d_{33}$ reflects the temperature where a structural instability starts. BMT-PT, BS-PT, BF-PT-La

Reports on mixed phases as a function of Temp:
- T+C in BZT-PT and BS-PT (coexistence range varying from $>100^\circ$ down to $5^\circ$ with increasing PT content. 111 invariant plane.
- $T_1+R \rightarrow T_1+T_2+R$ for BF-PT
  - Kothai et al. J. of Appl. Phys. 113, 084102 (2013);
Two volatile species = a more complicated world

What we learned from PZT, guides us but not always applicable the same way.

- Effect of dopants are material specific [i.e., Donor doping with volatile species (PZT) vs. non-volatile species (BaTiO₃)]
- $La_{Pb}^{*}, Nb_{Ti}^{*}$ does not have the same enhancements. Mn is the most successful dopant.
- $Zr_{Sc}^{*} = \text{not multi-valent, cannot be used in PZT as an alioivalent dopant.}$

Observations:

- Increased dielectric constant
- Lower temperature dependence of FE properties
- Square hysteresis loops
- Higher symmetry in bipolar measurements

"On the basis of vacancies facilitating domain boundary motion"

A. Sehirlioglu, et al., J. Amer. Soc. 93 [6], 1718, 2010
Two volatile species = a more complicated world

- **TGA**: Weight change in flowing oxygen/air for both doped and undoped ≈ -0.18%.
- **During sintering with sacrificial powder**: Undoped: -<2%, Doped: +0.15-0.3%.
- **Sintering atmosphere**: ≈ 90Pb-10Bi

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### Bismuth containing second phase

<table>
<thead>
<tr>
<th></th>
<th>%</th>
<th>R</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped</td>
<td>60</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>Doped</td>
<td>25</td>
<td>72</td>
<td></td>
</tr>
</tbody>
</table>

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A. Sehirlioglu, et al., J. Amer. Soc. 93 [6], 1718, 2010
Structure specific behavior?

\[ \approx 386 \, ^\circ\text{C} \]

- (1-2-3) and (4-5-6) Decreasing BS content, increasing PZ content, constant PT.
- (1-4), (2-5) and (3-6) Increasing PT content, decreasing PZ content, constant BS.
- (1-7-6) Decreasing BS content, increasing PT content, constant PZ.

Curie Temperature (°C)

- Rhombohedral / Constant PT
- Tetragonal / Constant PT
- 7 / Constant PZ

Weight change (%)

BS content (%)
Perovskite but which symmetry?

In BF-PT different ranges have been reported to be MPB (PT = 0.27-0.40 range)

- R and T ratio differences for same composition near MPB. Not observed away from MPB
- R phase crucial to keep the samples mechanically intact.
- Energy difference between R and T is small near MPB
- Local kinetic factors determine if metastable R will form.
- Samples are not inhomogeneous (microprobe/broadening)

- T1-T2 difference is the extent of hybridization
- R phase 11%→7% with temperature. (R3c)
- R+T needs to be shared in the same grain.

It was claimed to be due to sample prep.


BiScO$_3$-Bi(Zn,Zr)O$_3$-PbTiO$_3$

- Zn and Zr are ferroelectrically more active than Sc
- Average radius of (Zn$_{1/2}$,Zr$_{1/2}$) (73pm) is close to that of Sc (74.5pm)
- No increase in tetragonality due to existing Bi in the system

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<table>
<thead>
<tr>
<th></th>
<th>K</th>
<th>tan δ</th>
<th>$d_{33}$ (pm/V)$^*$</th>
<th>$k_p$</th>
<th>$Q_m$</th>
<th>$T_d$(°C)</th>
<th>$T_c$(°C)</th>
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<tbody>
<tr>
<td>BZZ2</td>
<td>780</td>
<td>0.017</td>
<td>526</td>
<td>0.45</td>
<td>38</td>
<td>382</td>
<td>422</td>
</tr>
<tr>
<td>PZT5A3</td>
<td>1910</td>
<td>0.013</td>
<td>982</td>
<td>0.507</td>
<td>64</td>
<td>354</td>
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$^*$Engineering high field $d_{33}$ values are measured using the same equipment/techniques

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- $25^\circ$C-150$^\circ$C
  - $E_c$ ≥ 20 → 10kV/cm
  - $P_R$ > 40μC/cm$^2$
BiScO$_3$-Bi(Zn,Zr)O$_3$-PbTiO$_3$

- PZT5A3 has depoled by 370 °C
- $Q_m$ has increased from 35 to 65 for BZZ2, a low value for $Q_m$ but a value equal to for PZT5A3 at room temperature.

**370 °C**

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<td>PZT5A3</td>
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<td>0</td>
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* $d_{33}$ values calculated from thickness mode
Doping of BiScO$_3$-Bi(Zn,Zr)O$_3$-PbTiO$_3$

- SIZZD- BZZ1-5BI (5BZZ-30BS-5BI-60PT), BZZ2-1Mn$_{\text{Ti}}$

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<td>422</td>
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<tr>
<td>1Mn(Ti)</td>
<td>610</td>
<td>0.005</td>
<td>304</td>
<td>0.34</td>
<td>100</td>
<td>382</td>
<td>421</td>
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<tr>
<td>SIZZD</td>
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<td>630</td>
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<td>13</td>
<td>342</td>
<td>398</td>
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*Engineering high field $d_{33}$ values
Doping of BiScO$_3$-Bi(Zn, Zr)O$_3$-PbTiO$_3$

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<td>422</td>
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<tr>
<td>1Mn(Ti)</td>
<td>4828</td>
<td>0.09</td>
<td>281</td>
<td>0.32</td>
<td>68</td>
<td>382</td>
<td>421</td>
</tr>
<tr>
<td>SIZZD+</td>
<td>6630</td>
<td>0.036</td>
<td>485</td>
<td>0.50</td>
<td>59</td>
<td>342</td>
<td>398</td>
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* $d_{33}$ values calculated from thickness mode
+ Data at 300°C for SIZZD

$Q_m = \frac{f_n^2}{2 \pi f_m Z_m C (f_n^2 - f_m^2)}$
Summary

• Increasing demand for high temperature piezoelectrics.
• $xBi(Me_1,Me_{II},...)O_3-(1-x)PbTiO_3$ solid solutions drive research.
• Factors that increase $T_c$ (c/a ratio, FE active cations) lead to difficulties in poling, increased dielectric losses and dc conductivity.
• Depoling Temperature
• Multiple volatile cations: Complicated charge compensation possible.
• Local inhomogeneties, local random fields.
• Relearning what we have learned from PZT.
• Initial breakthrough but minor improvements since then.
• However, lots of interesting science still waiting.

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