Recent advances in pyroelectric materials and their applications: People Counting, Cooling and Energy Harvesting

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Talk Synopsis

• Background to pyroelectrics
• Pyroelectrics – Applications in IR sensor arrays
  – Pyroelectrics as movement sensors
  – Example of an array-based “people sensor” system
  – Imaging Radiometry
• Pyroelectric ceramic materials for arrays
• Structured pyroelectric materials and MEMS devices
  – Functionally gradient pyroelectric ceramics
  – Radiation collection structures using thin films
• Electrocaloric effect in PZT thin films
• Pyroelectrics for Energy Harvesting
Pyroelectric and Electrocaloric Effects

\[ \Delta P_i = \left[ \frac{\partial D_i}{\partial T} \right]_{\sigma,E} \Delta T \]

\[ \Delta S = \left[ \frac{\partial S_i}{\partial E} \right]_{T,\sigma} \Delta E_i \]

\[ p_i = \left[ \frac{\partial D_i}{\partial T} \right]_{\sigma,E} = \left[ \frac{\partial S_i}{\partial E_i} \right]_{T,\sigma} \]
Pyroelectric Infrared Detectors

Pyroelectric Current: $I_p = A \cdot p \cdot dT/dt$

Pyroelectric Coefficient: $p = dP_s/dT$

Rate of change of element temperature with time
Schematic diagram of pyroelectric infra-red detector

Devices are “AC” coupled to radiation flux
Pyroelectric Thermal Sensor Arrays

In absence of chopper blade, a constant IR flux will lead to a constant pyroelectric temperature and no signal is produced. Non-chopped arrays “see” only moving warm (or cold) objects.

If imaging of static objects is required, a rotating chopper blade is included to modulate the IR onto the pyroelectric material.
Packaged Pyroelectric Array
People Sensing

Field of View

What the Array ‘Sees’
Supermarket checkout application (e.g. Tesco)

Allows managers a rapid and real-time summary of queue lengths and the ability to efficiently meet the “one in front” requirement.

“As a result, nearly a quarter of a million more customers every week don’t have to queue.” – Sir Terry Leahy CEO Tesco plc - 6th October 2006
Chopped operation
Gives thermal reading
Low cost
Applications to machine monitoring and process control

www.irisys.org

Imaging Radiometer
16x16
16x16 Interpolated to 128x128
Pyroelectric Ceramics
Important Properties Relevant to Pyroelectric Arrays

- Pyroelectric coefficient
- Dielectric properties
  - Dielectric constant
  - Dielectric loss
- Thermal properties
  - Specific heat
  - Density
  - Thermal conductivity
- Electrical Resistivity
- Piezoelectric properties
  - Determines microphonic noise, secondary & tertiary pyro effects

We also require:
- Good mechanical & chemical characteristics
- For focal plane preparation
  - Lapping/polishing
  - Metallisation
  - Photolithography
  - Reticulation
  - Hybridization technology
- Thin film devices
  - Require determination of properties in thin films
Functionally Gradient Pyroelectric Ceramics

• Design a ceramic structure to give a higher performance figure of merit.

Dense ceramic

Porous ceramic

Dense ceramic

Porous layer:

• Reduces average dielectric constant
• Reduces volume specific heat
• Introduces thermal barrier – reduces thermal diffusivity
Functionally Gradient Pyroelectric Ceramics - Manufacture

Functionally graded tri-layer structure

Fabricated by lamination of tape cast layers
Theoretical Analysis

Permittivity:

Bruggeman Model\(^1\):

\[
\varepsilon_L = \varepsilon_D \left(1 - \frac{3}{2} \left(\frac{P_L}{\varepsilon_D}\right)\right)
\]

Pyroelectric effect:

Assume pyroelectric effect is proportional to the volume of pyroelectric material between the electrodes

\[
P_A = P_D \left(1 - \frac{P_A}{P_D}\right)
\]

\(\varepsilon_D, P_D\) = permittivity, pyro coefficient of fully-dense ceramic

Functionally graded tri-layer structure - properties

Variation of $F_V$ with porosity in tri-layer structure

Pyroelectric Thin Films & MEMS Structures
Integrated Arrays using Ferroelectric Thin Films

- Low cost
- Thin films (low thermal mass)
- Excellent isolation
- High performance

Requires high quality ferroelectric thin films at low deposition temperatures (<550°C for survival of Al/Si metallisation)
Sol gel PZT and PMZT thin films

XRD pattern showing high degree of 111 orientation of PZT and PMZT films on 111 Pt electrode

FIB / TEM image showing the epitaxial growth of the (111) PMZT film on the (111) electrode

Five layers of Mn (1%) -doped PZT (30/70), thickness=400nm processed on hot plate at 530 to 560°C
### Dielectric (33Hz) and Pyroelectric Properties of PZT and PMZT (M=1%Mn) Films

<table>
<thead>
<tr>
<th></th>
<th>PZT3070</th>
<th>PMZT3070</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dielectric Constant</td>
<td>375</td>
<td>260</td>
</tr>
<tr>
<td>Dielectric Loss (%)</td>
<td>1.61</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Mn doping leads to a significant reduction in dielectric constant and loss and hence a large improvement in the pyroelectric FD. Best FD is equivalent to bulk pyroelectric ceramics.


Pyroelectric coefficient

- PZT3070: 2.11
- PMZT3070: 3.52 \( \times 10^{-4} \) (C/m²K)

Figure of Merit \( F_D \) (33Hz)

- PZT3070: 1.15
- PMZT3070: 3.85 \( \times 10^{-5} \) (Pa⁻⁰.⁵)

\[
F_D = \frac{p}{c' \sqrt{\varepsilon \varepsilon_0 \tan \delta}}
\]

NB: All dielectric properties measured at low frequencies 33-100Hz
Pyro IR Detectors with Integrated Radiation Collectors

- It is not possible for the active area of the thermal detector to fill the available space in the pixel because of the need for good thermal isolation (long legs).
- Exploit the principle of the non-imaging radiation collector in order to collect the radiation from an area close to that of the full pixel down onto the active area of the detector.
- Smaller active areas will give higher specific detectivity, if the radiation is collected from a larger area into a detector with small thermal mass.

![Schematic of Concept]

Radiation collector cavities
HARM micromachined silicon wafer
Pyroelectric element
Conductive Bump

Incident IR
Si Readout IC
CPC Cavity Device Structures

Optical micrographs showing the detector structures and contact areas. Note the thermal isolation structure defined for the sensitive area.

SEM cross section of detector structure with isotropically-etched cavity.

Collection efficiency of x2 demonstrated.

Giant Electrocaloric Effects in Ferroelectric Thin Films
PZT Phase Diagram – Near PbZrO₃

- \( A₀ \rightarrow F_{R(HT)} \) Transition (Heating)
- \( F_{R(HT)} \rightarrow A₀ \) Transition (Cooling)
- \( F_{R(HT)} \rightarrow F_{R(HT)} \) Transition
- \( F_{R(LT)} \rightarrow A₀ \) Transition
- \( F_{R(HT)} \rightarrow P₃ \) Transition (Ceramics)
- \( F_{R(HT)} \rightarrow P₃ \) Transition (Crystals)

A. 280°C
B. 220°C
C. 145°C
D. 35°C
Electro-caloric Effects in PZT95/5 Films

Temperature change can be calculated from:

\[
\Delta T = -\frac{1}{c'} \int_{E_1}^{E_2} T \left( \frac{\partial P}{\partial T} \right)_{\sigma,E} dE
\]

Previous highest \(\Delta T=2.5\)K in \(\text{Pb}_{0.99}\text{Nb}_{0.02}(\text{Zr}_{0.75}\text{Sn}_{0.20}\text{Ti}_{0.05})\text{O}_3\) ceramics at 750V (30kVcm\(^{-1}\))
Why is Effect so big?

• Electric fields that can be applied to a thin film are much greater than can be obtained in the bulk (480kV/cm cf 30kV/cm)

• PZT95/05 sits at a very interesting point in the phase diagram
  – Tricritical behaviour in the $F_{R(HT)}$ to $P_C$ Transition$^1$
  – Change from $A_O$ to $F_{R(LT)}$ phase at room temperature

Pyroelectric Energy Harvesting

• Depends upon cycling clockwise around the P-E loop.

The Ericsson or “Olsen” cycle (shown here for a \( \text{Pb}_{0.99}\text{Nb}_{0.02}(\text{Zr}_{0.68}\text{Sn}_{0.25}\text{Ti}_{0.07})_{0.98}\text{O}_3 \) (PNZST) Ceramic)\(^1\)

A-B: Isothermal (low T) \( \uparrow \) in E & P
B-C: \( \uparrow \) in T at constant E, \( \downarrow \) in P
C-D: \( \downarrow \) in E & P
D-C: \( \downarrow \) in T at constant E, \( \uparrow \) in P

Pyroelectric Energy Harvesting

- Other cycle types

**Stirling cycle**

**Resistive cycle**
## Pyroelectric Energy Harvesting

### Observed Performances (Ceramics)

<table>
<thead>
<tr>
<th>Material</th>
<th>Cycle Type</th>
<th>$T_{\text{min}}$ °C</th>
<th>$T_{\text{max}}$ °C</th>
<th>$E_{\text{min}}$ MVm$^{-1}$</th>
<th>$E_{\text{max}}$ MVm$^{-1}$</th>
<th>Max Energy per cycle mJcm$^{-3}$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNZST Ceramic</td>
<td>Ericsson</td>
<td>158</td>
<td>170</td>
<td>0.4</td>
<td>2.8</td>
<td>95‡</td>
<td>1</td>
</tr>
<tr>
<td>PNZST Ceramic</td>
<td>Stirling</td>
<td>158</td>
<td>170</td>
<td>0.4</td>
<td>2.8</td>
<td>67</td>
<td>1</td>
</tr>
<tr>
<td>PNZST Ceramic</td>
<td>Resistive</td>
<td>158</td>
<td>170</td>
<td>0.4</td>
<td>2.8</td>
<td>26</td>
<td>1</td>
</tr>
<tr>
<td>PNZST Ceramic</td>
<td>Ericsson</td>
<td>145</td>
<td>175</td>
<td>0.8</td>
<td>3.2</td>
<td>300</td>
<td>2</td>
</tr>
<tr>
<td>PMN/PT 90/10 Ceramic</td>
<td>Ericsson</td>
<td>35</td>
<td>85</td>
<td>0.5</td>
<td>3.5</td>
<td>186</td>
<td>3</td>
</tr>
<tr>
<td>PLZT 8/65/35 Ceramic *</td>
<td>Ericsson</td>
<td>25</td>
<td>160</td>
<td>0.2</td>
<td>7.5</td>
<td>888</td>
<td>4</td>
</tr>
</tbody>
</table>

Refs:

‡At an efficiency of 15% of Carnot

*Produced a power output of 15.8mWcm$^{-3}$ at 0.02Hz
**Pyroelectric Energy Harvesting**

**Predicted Performances (Thin Films)**

<table>
<thead>
<tr>
<th>Material</th>
<th>Cycle Type</th>
<th>T °C</th>
<th>E MVm⁻¹</th>
<th>Max Energy per cycle mJcm⁻³</th>
<th>$\eta / \eta_{Carnot}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMN/PT 90/10</td>
<td>Ericsson</td>
<td>75</td>
<td>90</td>
<td>432</td>
<td>34</td>
</tr>
<tr>
<td>PZT95/05</td>
<td>Ericsson</td>
<td>220</td>
<td>78</td>
<td>596</td>
<td>54</td>
</tr>
</tbody>
</table>


Pyroelectric Energy Harvesting

• 100’s mJcm⁻³ per cycle can be extracted for temperature variations of a few 10’s °C
• Operational range RT to 100’s °C
• Efficiencies (15 to 50% of Carnot) significantly higher than thermoelectrics
• Oxide ceramics, (crystals), polymers & thin films all possible candidates
• Issues: cracking (oxides), breakdown, high field requirements (polymers and thin films), need a mechanism to convert a T difference into a T variation
Conclusions

• Pyroelectric arrays offer excellent capabilities, especially for people sensing.

• The versatility of pyroelectric ceramics, with control of their properties through chemical doping, offers great advantages in array fabrication.

• There is little prospect for radical improvement in pyroelectric figures of merit with conventional pyroelectric materials, but new ideas such as using functionally-gradient materials may offer a way around this impasse. Significant improvements in $F_V$ have been demonstrated.

• PMZT3070 thin films with excellent pyroelectric properties ($F_D=38.5\mu Pa^{-1/2} –$ equivalent to the bulk) have been demonstrated. Controlled introduction of porosity can give figure-of-merit improvements, as with bulk materials.

• The giant electrocaloric effect in thin films is an interesting new direction with possibilities for cooling and energy harvesting.