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Pyroelectric Response in $Hf_{1-x}Zr_xO_2$ Thin Films

Sean W. Smith, Andrew Kitahara, Michael D. Henry, Michael T. Brumbach, Mark A. Rodriguez, and Jon F. Ihlefeld

Sandia National Laboratories

Albuquerque, NM USA

Ssmith5@sandia.gov

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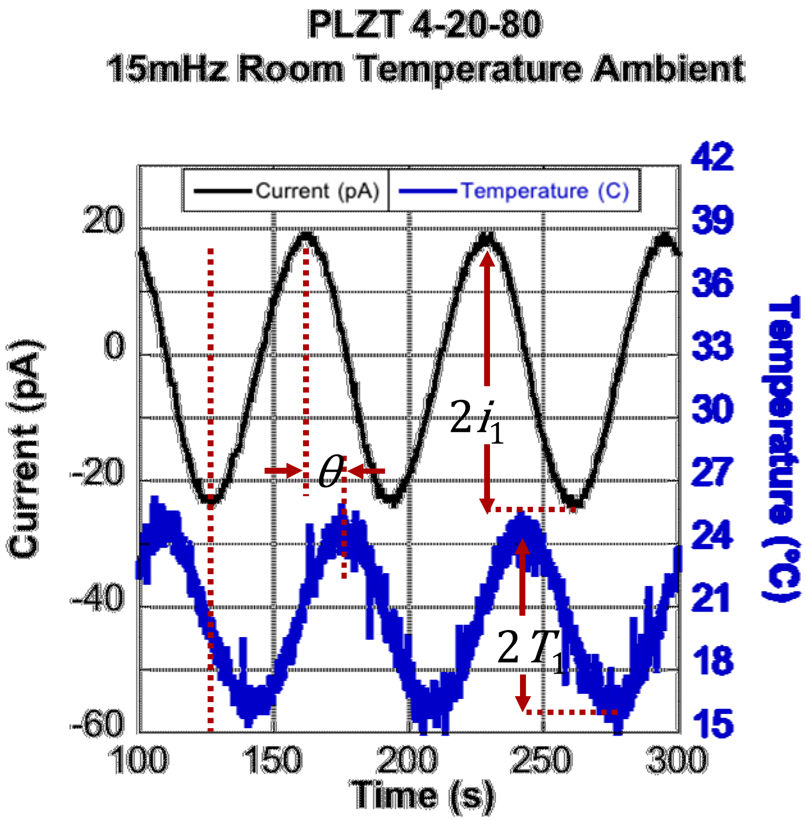
Doped HfO_2 Pyroelectric Response

- Ferroelectric with permanent polarization must have a pyroelectric response
- Park *et al*. Nano Energy 2014
  - Antiferroelectric Zr rich $Hf_{1-X}Zr_XO_2$ ($0.7 \leq X \leq 0.9$)
  - Measured Polarization-Electric field hysteresis curves at various Temperatures
- Hoffman *et al.* Nano Energy 2015
  - $Si{:}HfO_2$
  - Measured pyroelectric coefficient due to orthorhombic to tetragonal phase change
  - Pyroelectric current measured while sample temperature increased
- These methods can be influenced by extrinsic artifacts such as leakage current.

Park *et al*., Nano Energy **12**, 131 (2015) Hoffman *et al*., Nano Energy **18**, 154 (2015)

Pyroelectric Measurements

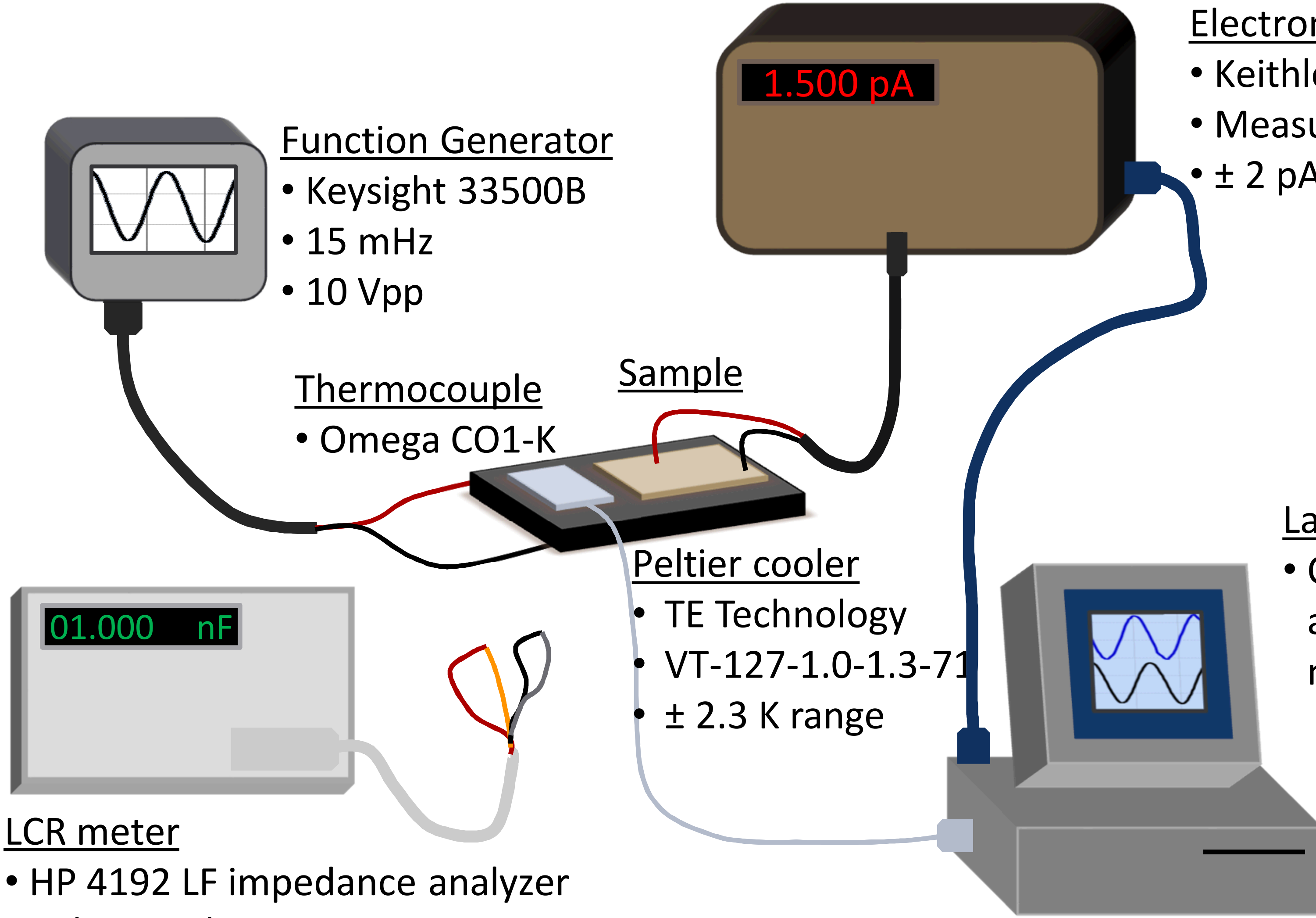
- Static/Indirect
  - Static: Discrete temperatures
    - Charge compensation by leakage current
  - Indirect: Measure another physical parameter *i.e.* polarization
    - Incomplete switching or fatigue
- Dynamic
    - Continuous change in temp and measure of current
  - Linear temperature – (Byer-Roundy)
    - Difficult to separate pyroelectric and other thermally induced currents
  - Oscillating temperature
    - Pyroelectric current depends on change in temperature with time



$$i_1 \sin(\theta) = pA\omega T_1$$

p – pyroelectric coefficient
ω – angular frequency of temperature
A – area of device

Pyroelectric Setup



Function Generator
- Keysight 33500B
- 15 mHz
- 10 Vpp

Electrometer
- Keithley 6512
- Measures current
- ± 2 pA range

Thermocouple
- Omega CO1-K

Sample

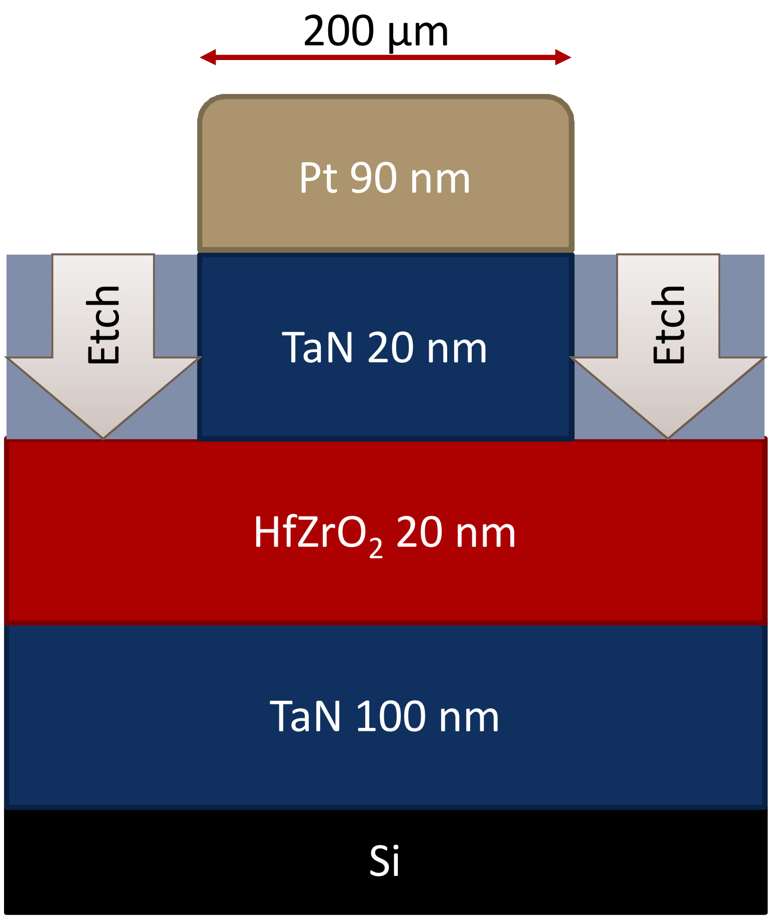
Peltier cooler
- TE Technology
- VT-127-1.0-1.3-71
- ± 2.3 K range

Labview
- Collects current and temperature measurement

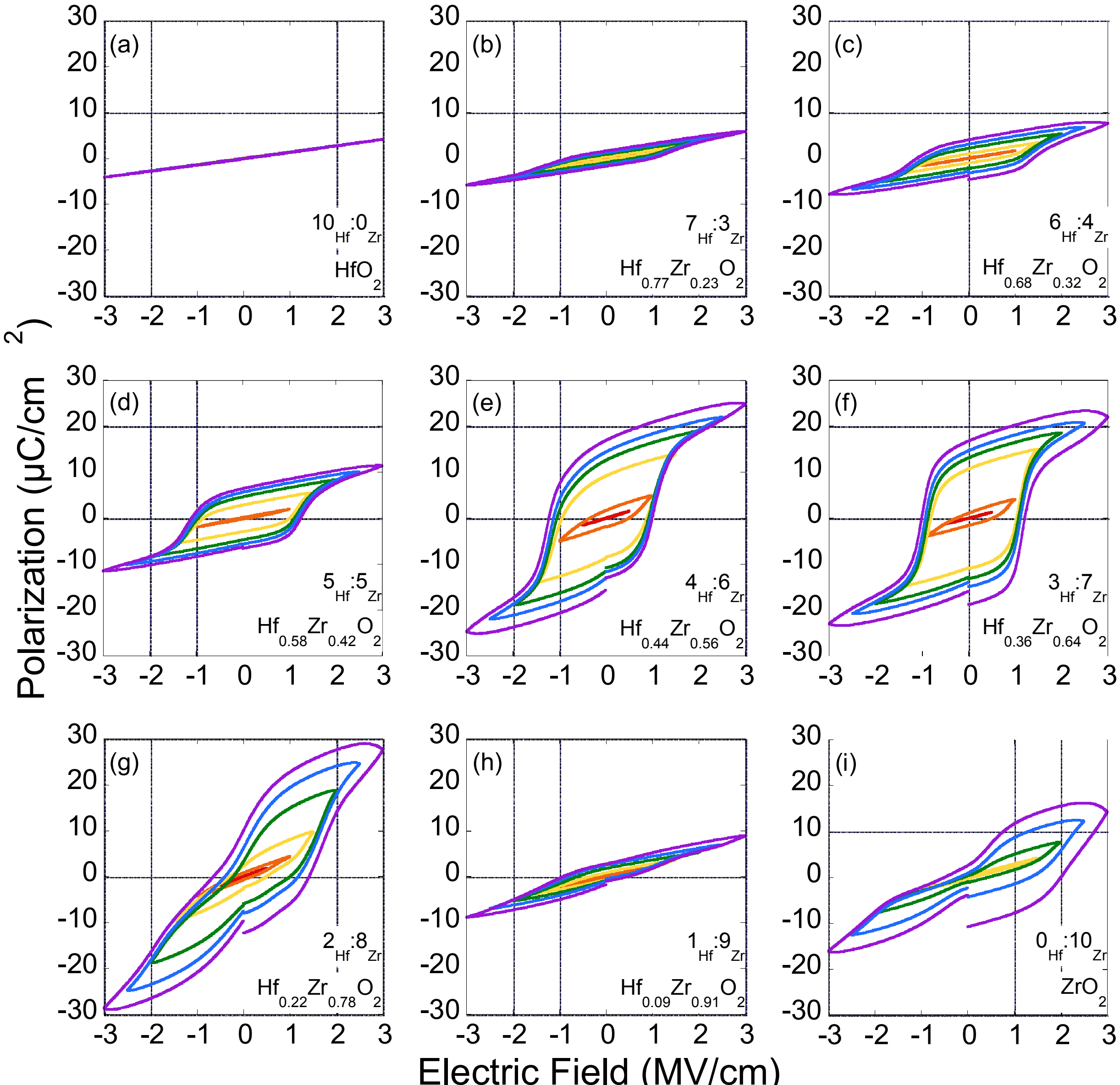
LCR meter
- HP 4192 LF impedance analyzer
- Pole sample 4V
- Check capacitance and loss tangent at 1 kHz

Experimental and Device Stack

- RF sputter TaN from TaN target
- Thermal ALD $Hf_{1-X}Zr_XO_2$ at 150 °C by TDMA Hf, TDMA Zr, and H_2O
  - Cycle ratio to control composition
- RF sputter blanket TaN cap
- Rapid thermal anneal 30s at 600 °C under nitrogen
- Sputter Pt through shadow-mask
- ICP reactive ion etch
  - SF_6 and C_4F_8 atmosphere

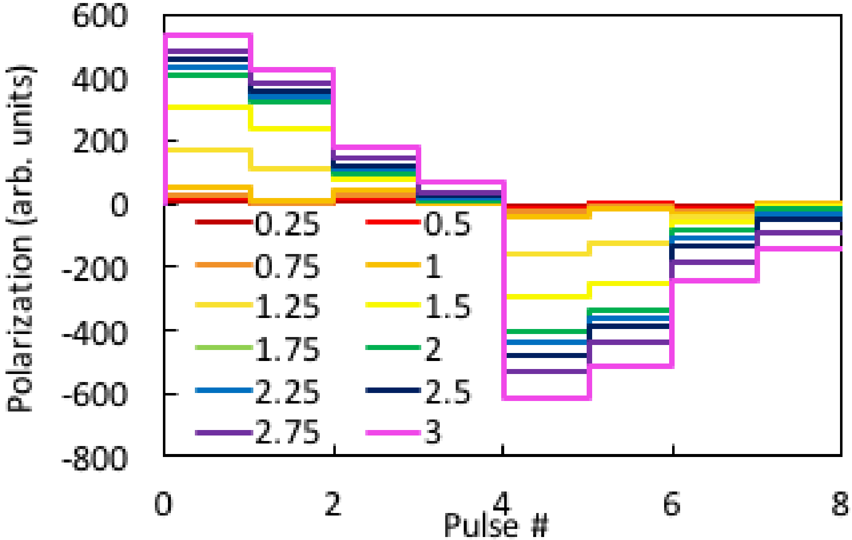


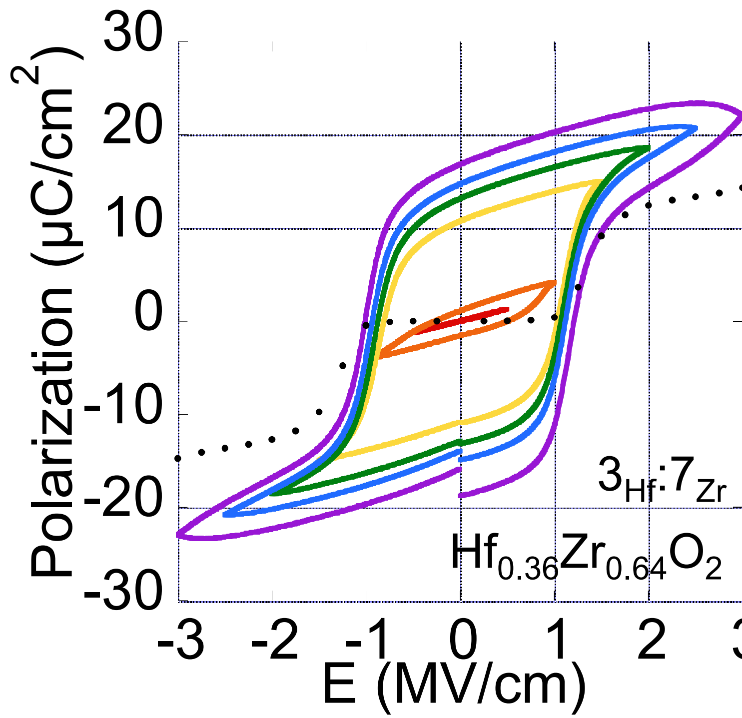
Polarization Electric Field Loops



- Composition measured by XPS
  - HfO_2 rich due to larger HfO_2 growth per cycle.
- Trend similar to literature.
  - Antiferroelectric consistent with ZrO_2
- Polarization does not saturate due to leakage current

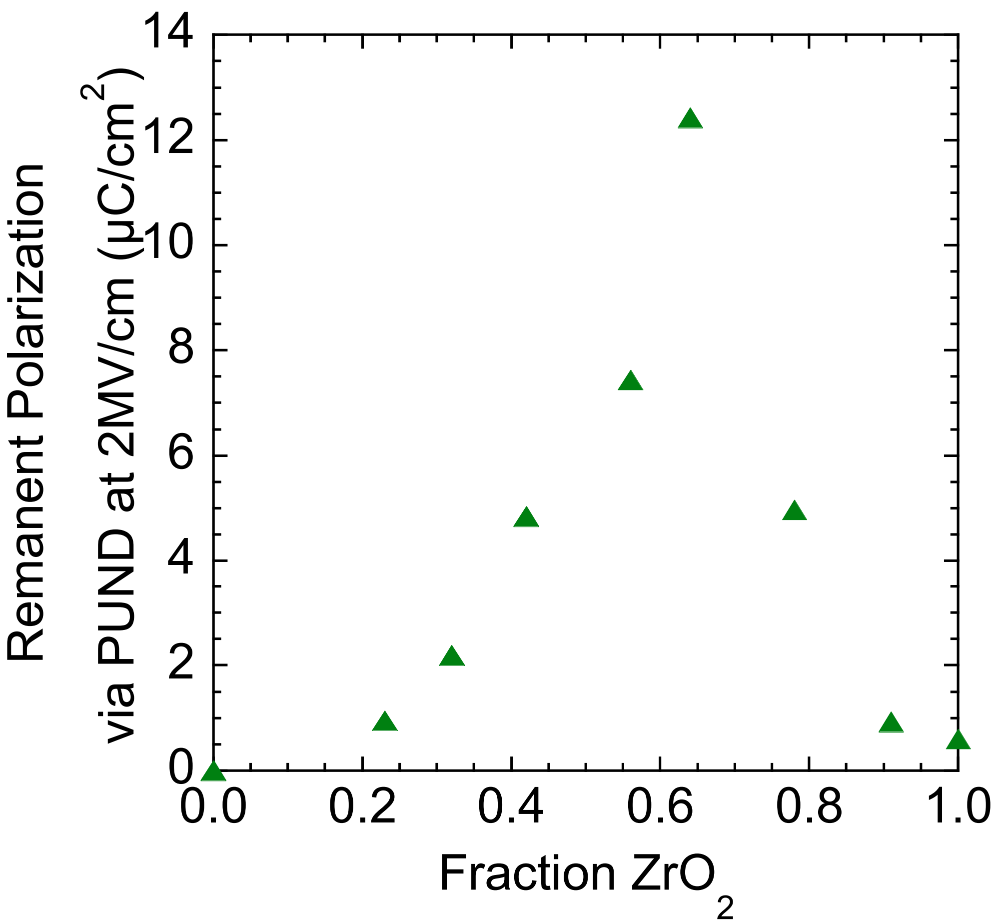
Pulsed Positive Up Negative Down





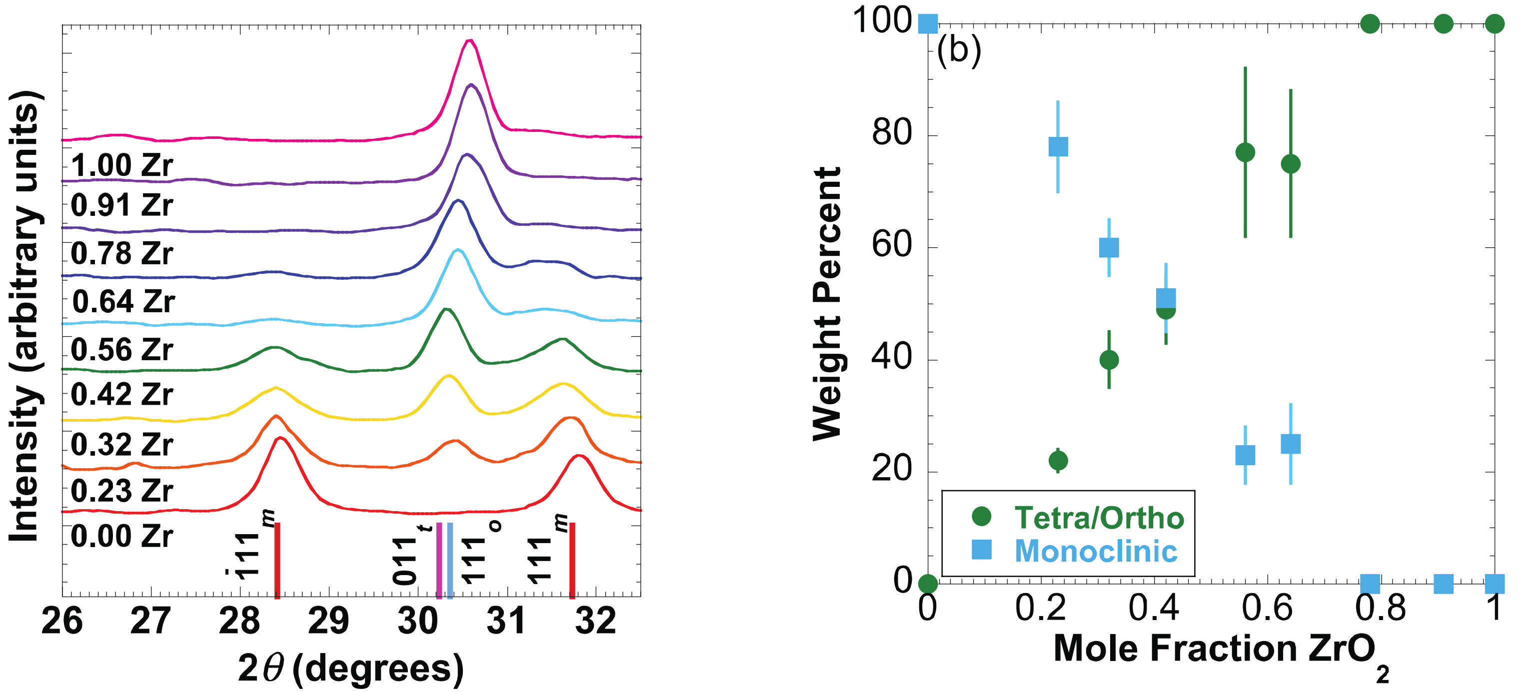
- PUND Remanent Polarization
  - doesn't saturate with E.
  - consistently less than Polarization measured at 0 MV/cm.
  - Follows trend closely

Pulsed Positive Up Negative Down



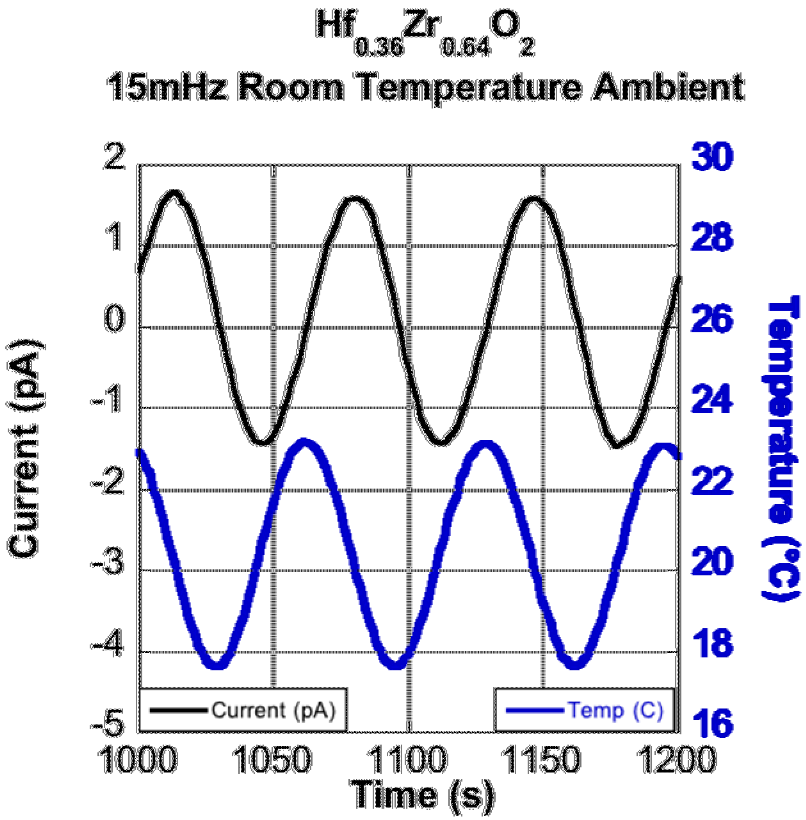
- Remanent polarization at 2 MV/cm via PUND
- Follows similar trend to PE loops
- Increasing R_P with fraction ZrO_2 up to 0.64

GIXRD: Phase Assemblage

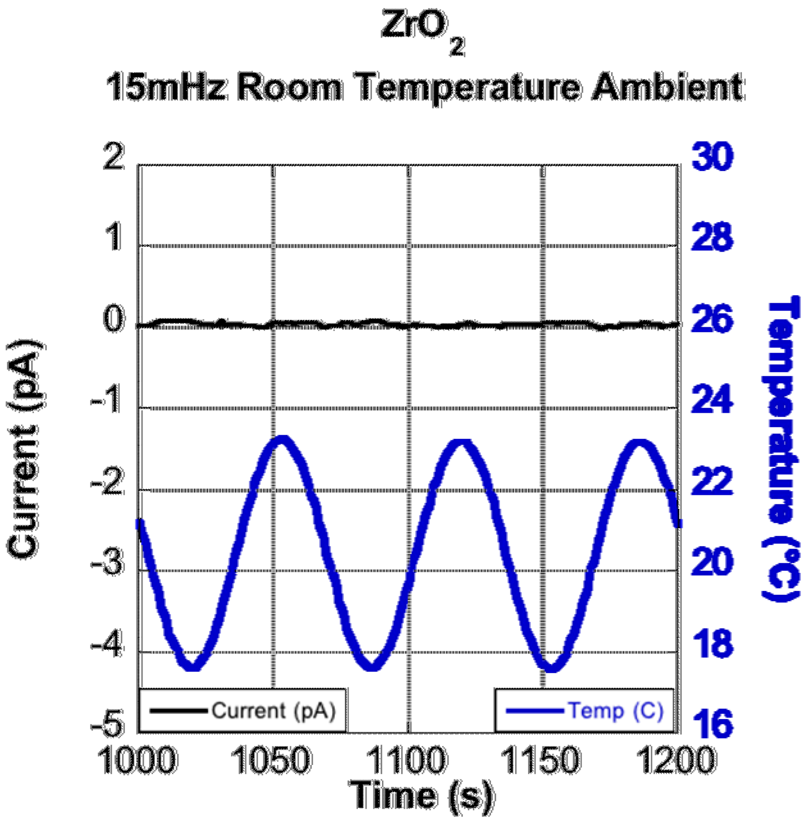


- Monoclinic peaks decrease and Orthorhombic/Tetragonal increase with increased Zr content
- $011_t/111_o$ peak shifts to higher angles with increased Zr content
- Orthorhombic/tetragonal intensity correlates with polarization response

Pyroelectric Waveforms



Pyroelectric current measurement for $Hf_{0.36}Zr_{0.64}O_2$ film.
J_{MAX}= 1.33 x10^{-9} Acm^{-2}
ΔT= ±2.8 K
p= 48 μ$Cm^{-2}K^{-1}$
θ = 94°



Pyroelectric current measurement for ZrO_2 film.
J_{MAX}= 6.2 x10^{-11} Acm^{-2}
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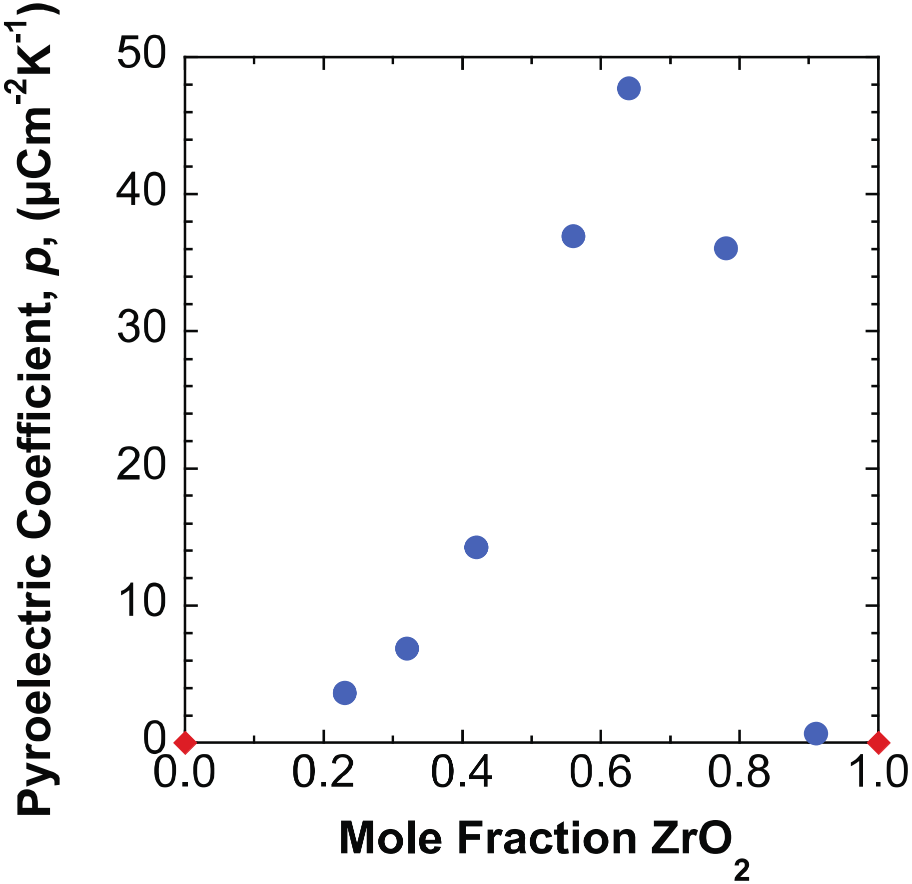
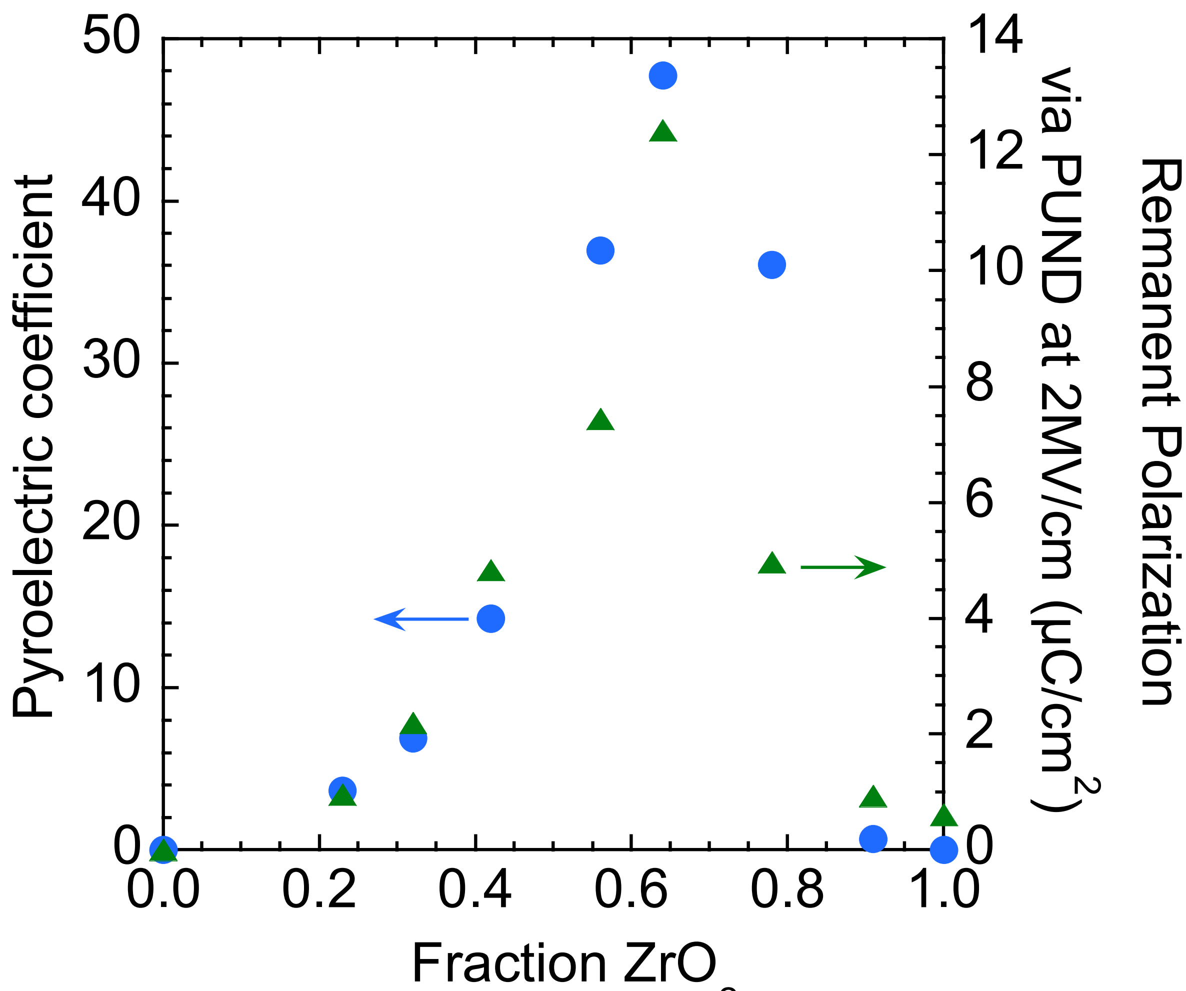
Pyroelectric Coefficients



Room temperature pyroelectric coefficient for $Hf_{1-x}Zr_xO_2$ films as a function of Zr content.

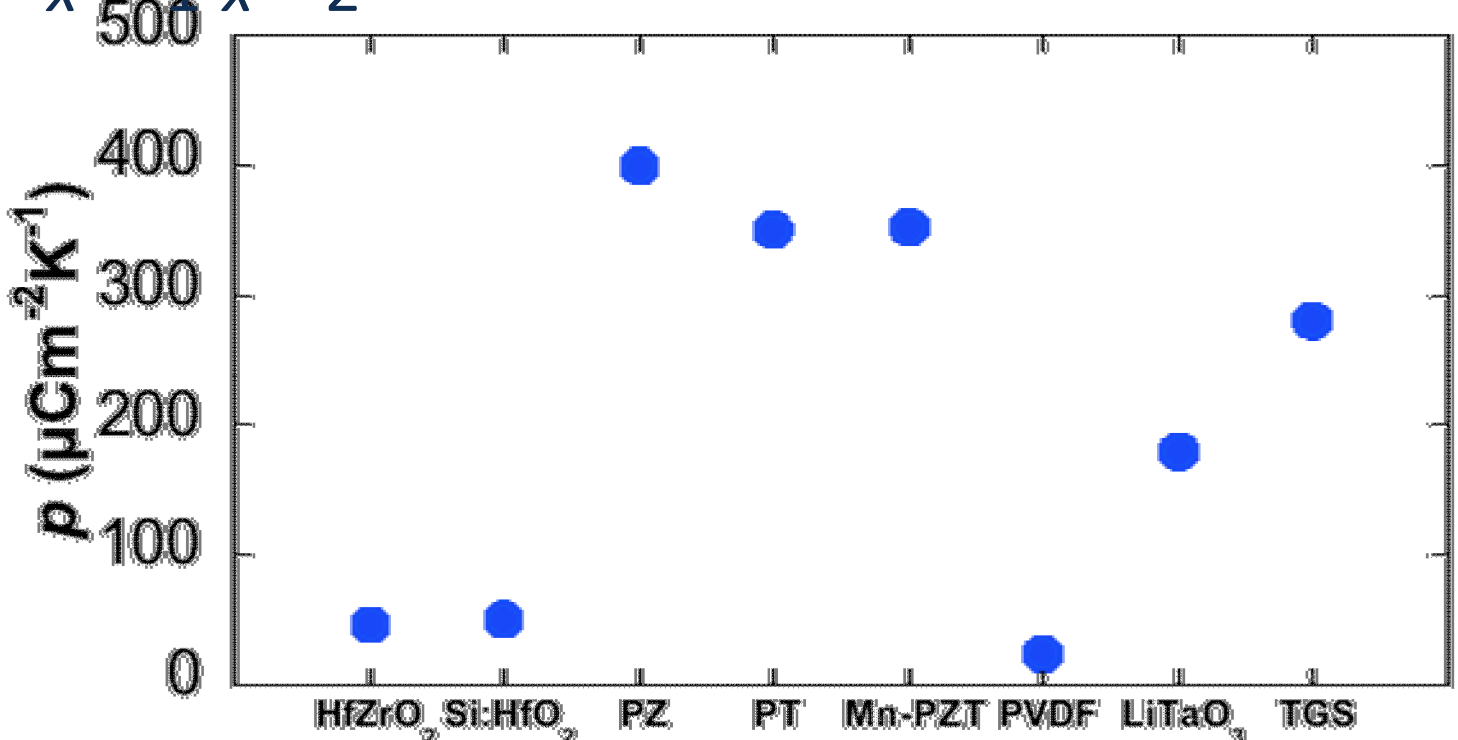
- Pure HfO_2 and ZrO_2: no pyroelectric response
- Increasing pyroelectric coefficient with Zr content
  - Maximum: 48 $\mu Cm^{-2}K^{-1}$ at 64% ZrO_2
- Follows polarization and orthorhombic phase content trend.

Pyroelectric Coefficients



Room temperature pyroelectric coefficient and PUND measured remanent polarization at 2 MV/cm for $Hf_{1-x}Zr_xO_2$ films as a function of Zr content.

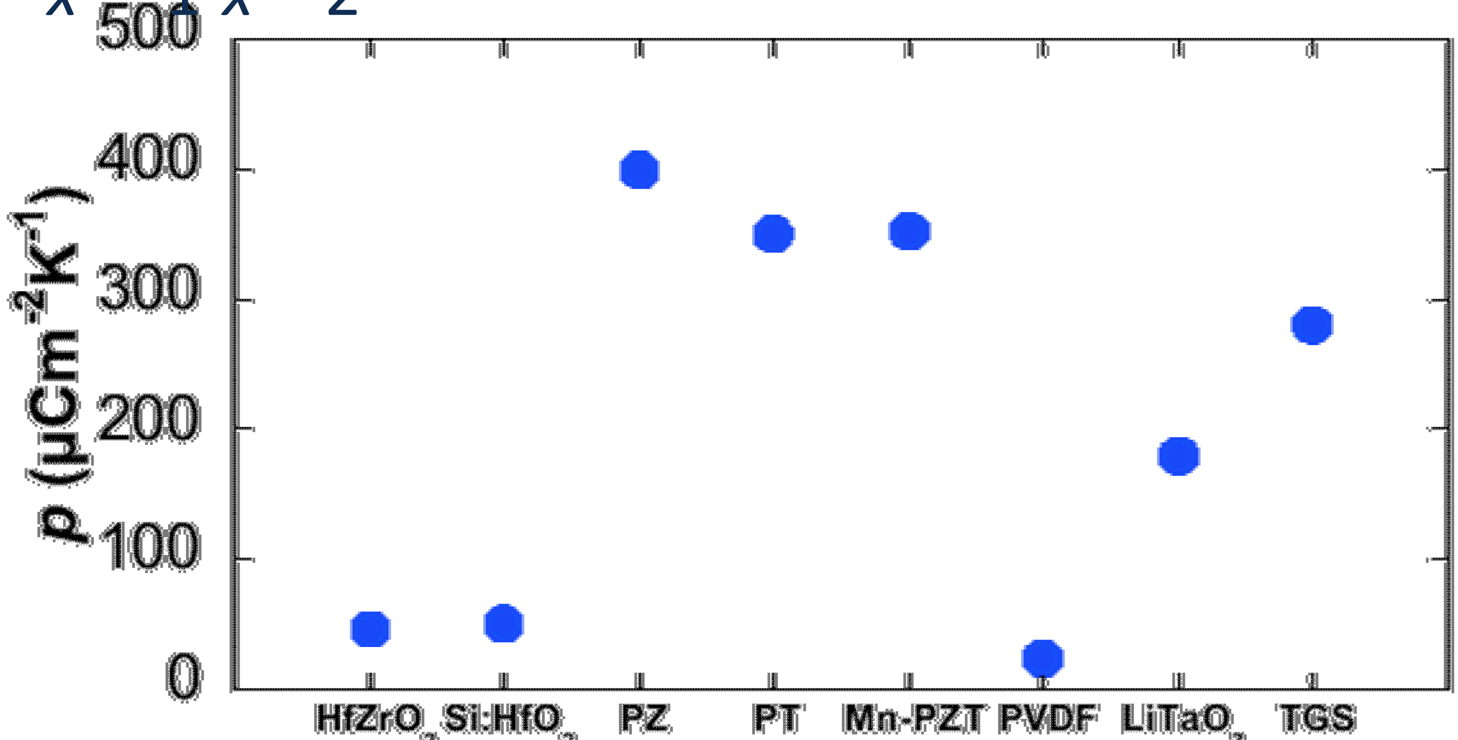
$Hf_xZr_{1-x}O_2$ & Other Materials



Material	p	Dielectric properties		F_I 10^{-10}	F_V	F_D 10^{-6}	Reference
	($\mu Cm^{-2}K^{-1}$)	ε_R	tan δ	(mV^{-1})	(m^2C^{-1})	($Pa^{-1/2}$)	
$Hf_{0.32}Zr_{0.68}O_2$	48	25	0.014	0.22	0.10*	13*	This work
5.6 mol% Si:HfO_2	52	38	0.025	0.20	0.06	7	Hoffmann 2015 *Nano Energy*
Mod. PZ	400	290	0.003	0.02	0.06	58	Whatmore 2004 *J Electroceramics*
Mod. PT	350	220	0.01	0.01	0.07	32	
Mn -PZT thin film	352	257	0.007	-	-	39	Sebald 2008 *IEEE Trans.*
PVDF	25	9	0.03	0.11	0.14	7	Ploss 1991 *Sensors and Actuators A*
$LiTaO_3$	180	47	0.005	0.56	0.14	39	
TGS	280	38	0.01	1.2	0.36	66	

* Literature value bulk heat capacity

$Hf_xZr_{1-x}O_2$ & Other Materials



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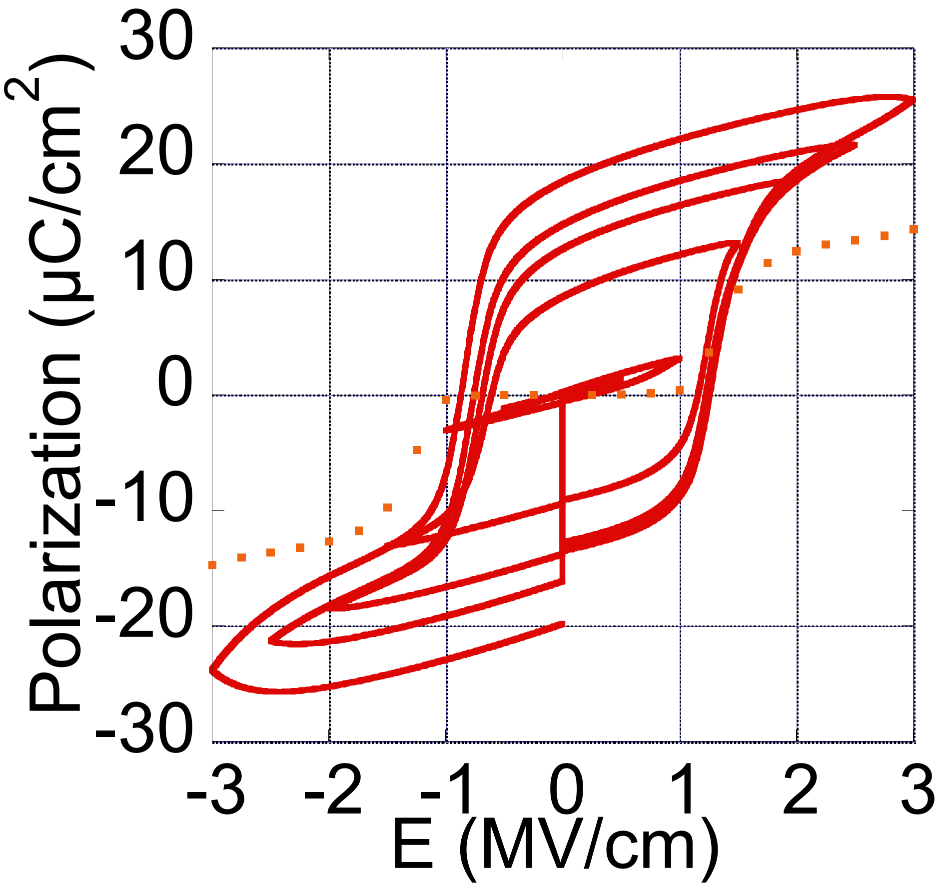
Conclusions

- We do observe a pyroelectric response in $Hf_{1-X}Zr_XO_2$
  - Consistent with permanent polarization
  - Consistent with ferroelectricity
- Pyroelectric response, polarization magnitude, orthorhombic/tetragonal phase intensity, are all correlated with composition.
- $Hf_{0.36}Zr_{0.64}O_2$ pyroelectric coefficient and IR detector figures of merit similar to PVDF and $LiTaO_3$
  - p=48 $\mu Cm^{-2}K^{-1}$
  - F_I= 0.22 mV^{-1}
  - F_V= 0.10 m^2C^{-1}
- This could be a promising material for large area IR detectors or low frequency detection.

BONUS SLIDES

PUND



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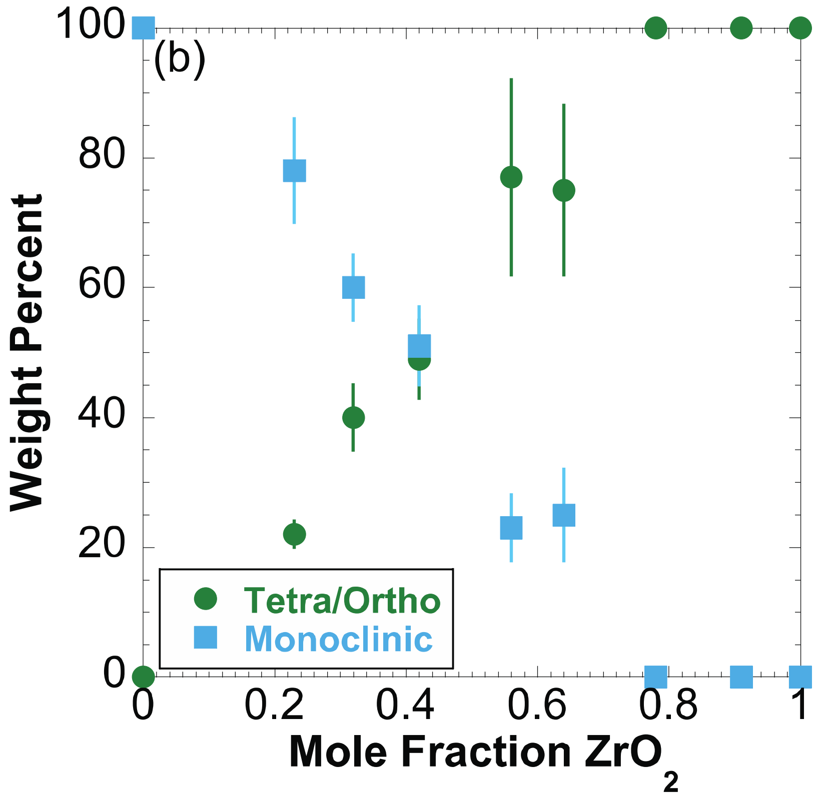

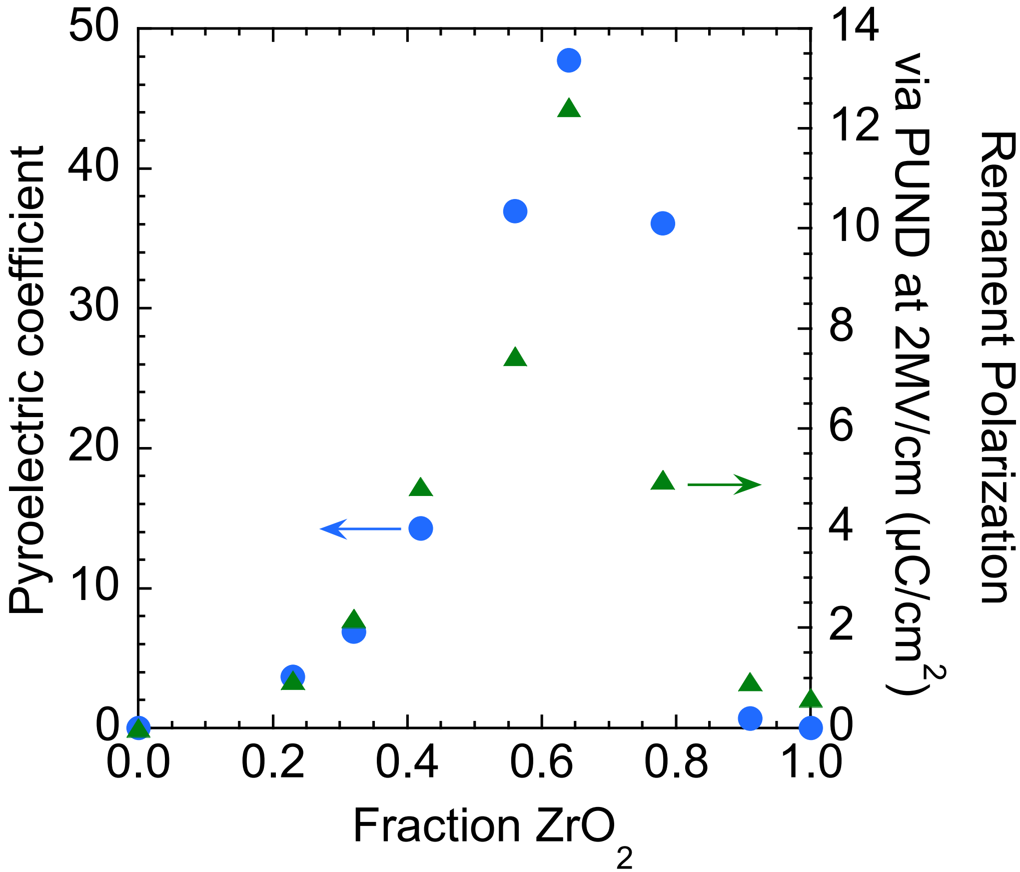

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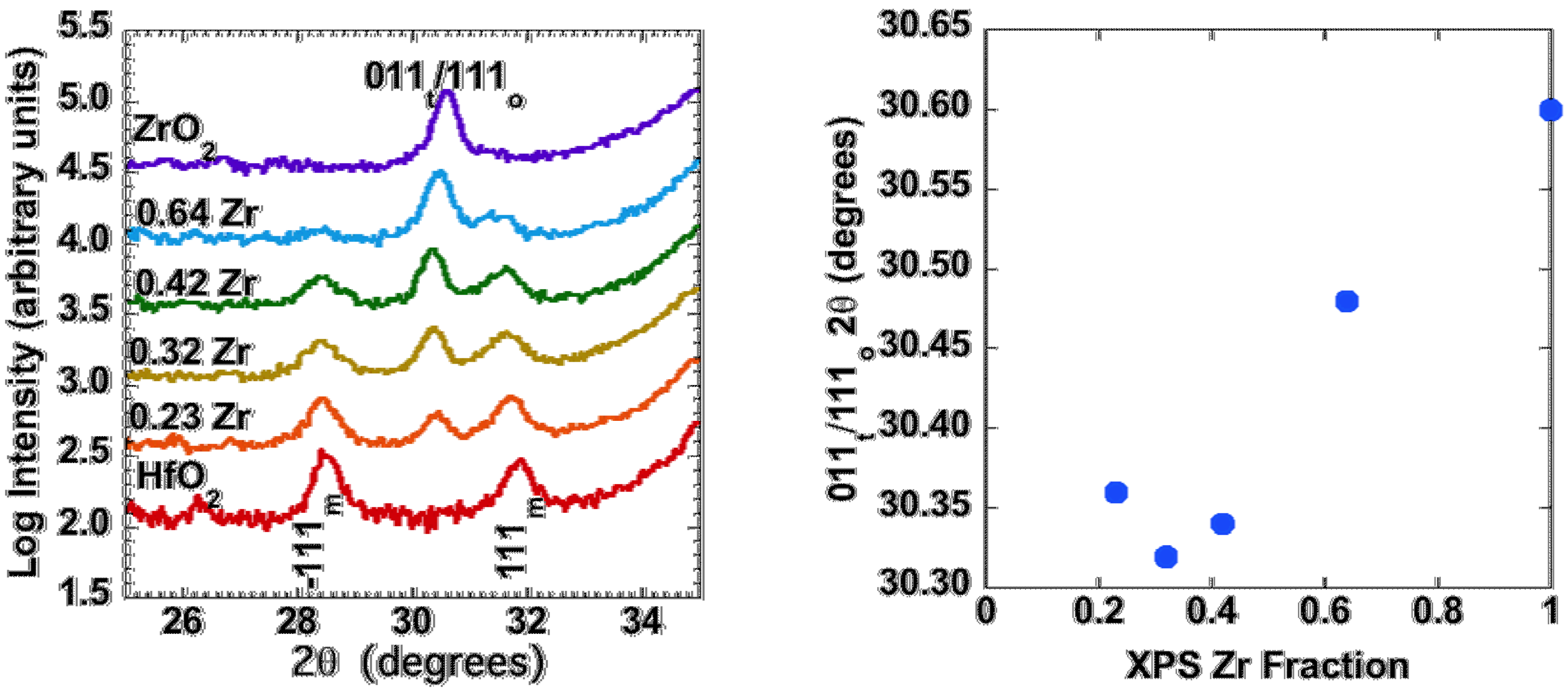

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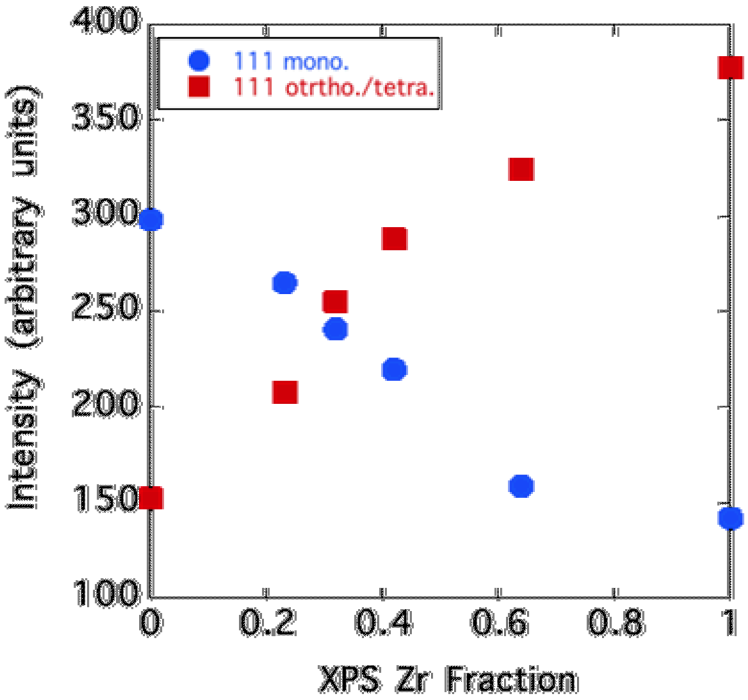
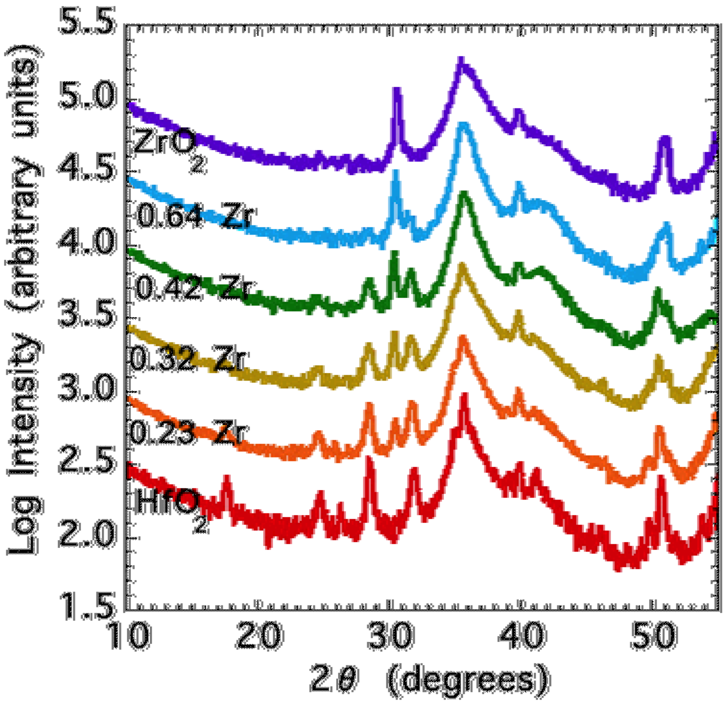
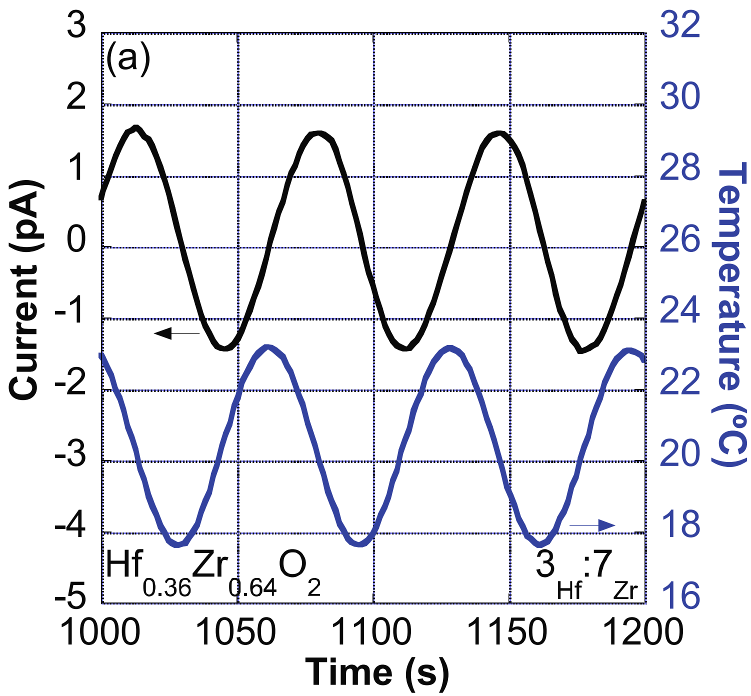
X-ray results





Pyroelectric Waveforms



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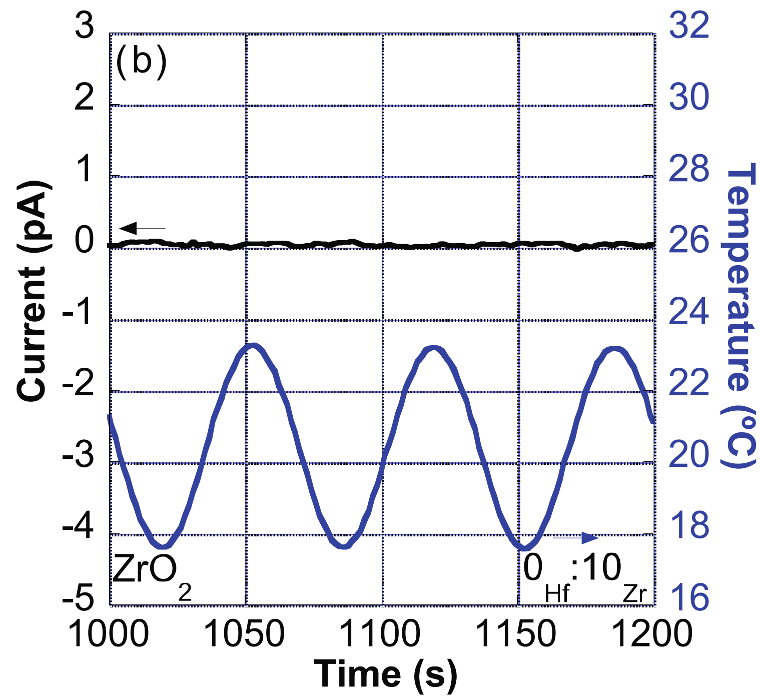

Pyroelectric current measurement for ZrO_2 film.

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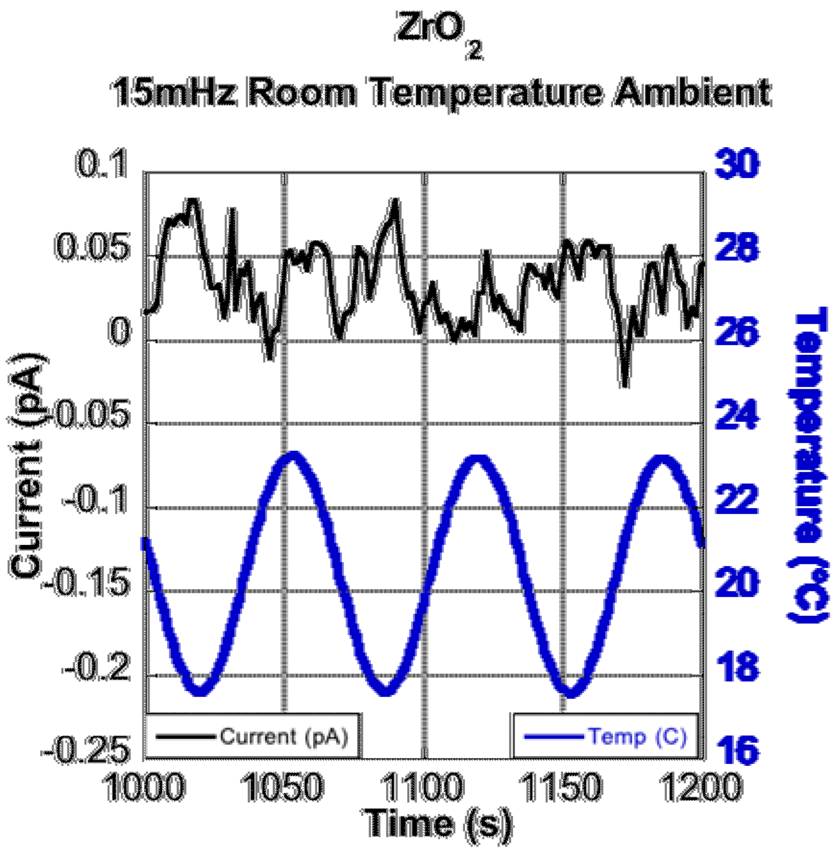
p= NA

ZrO_2 pyro waveforms zoomed in



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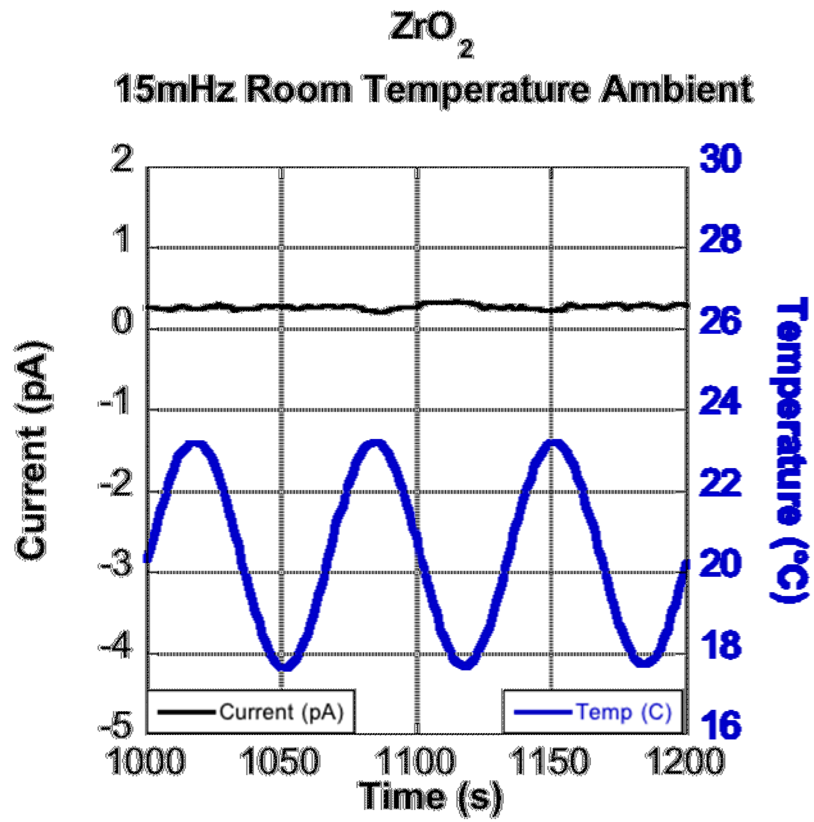

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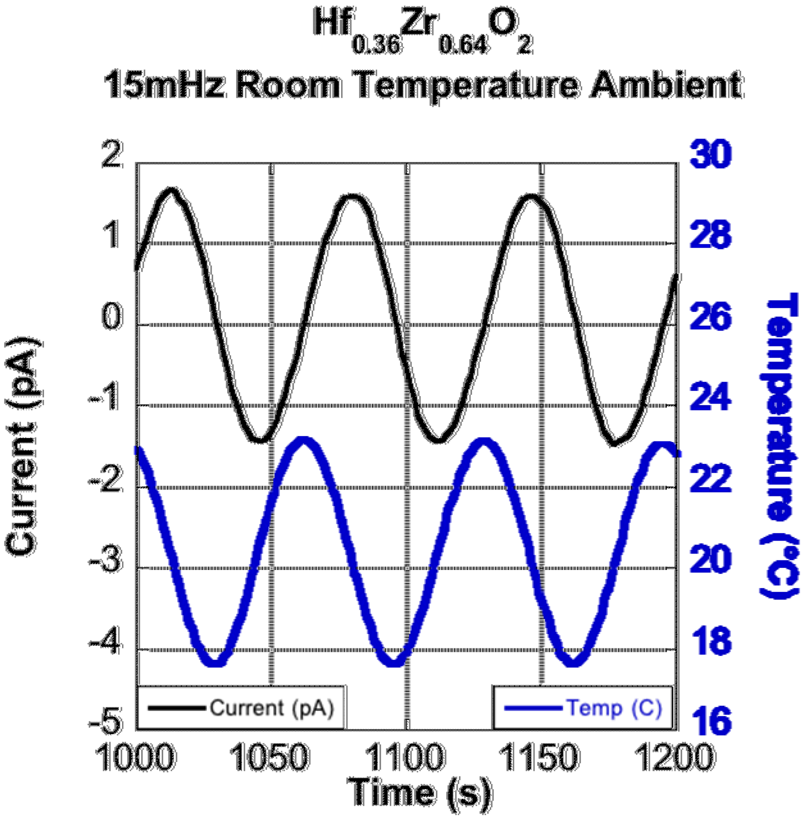
Pyroelectric Waveforms



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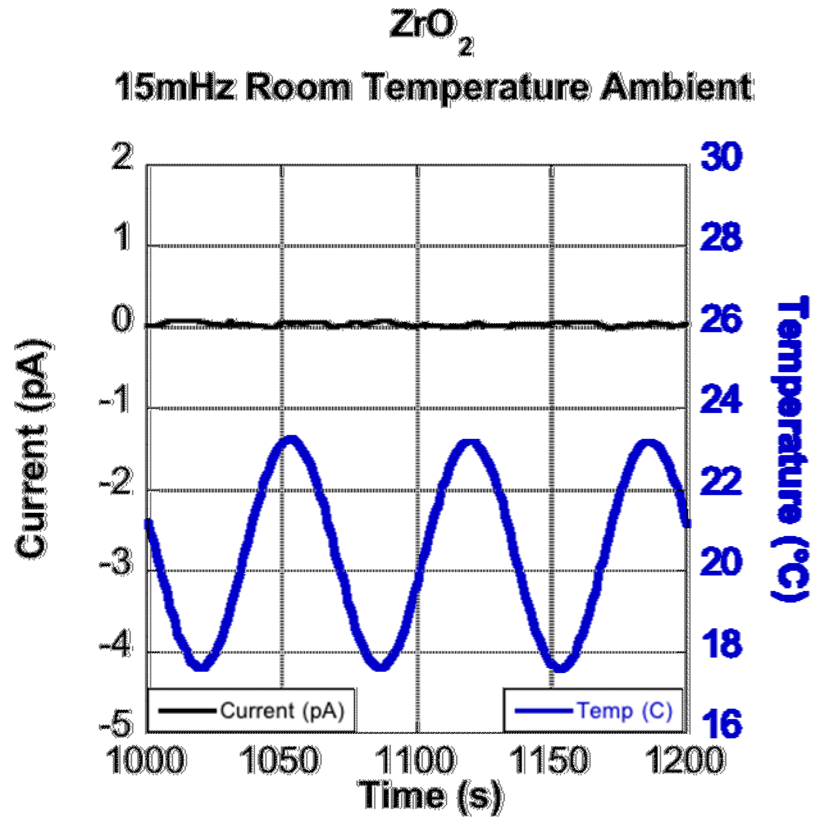

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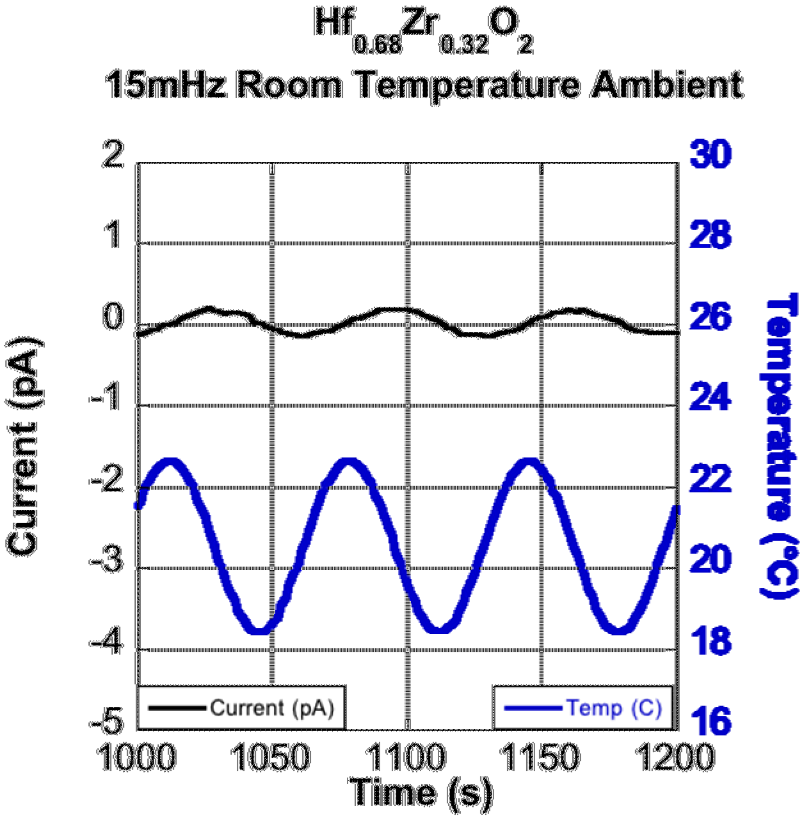
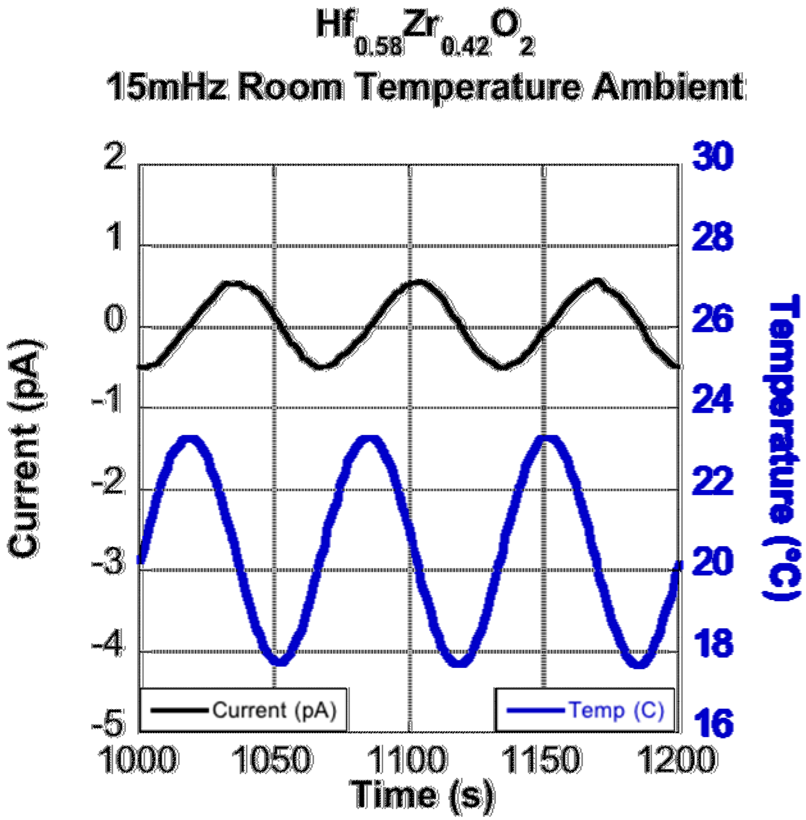
Pyroelectric Waveforms



Pyroelectric current measurement for $Hf_{0.68}Zr_{0.32}O_2$ film.
J_{MAX}= 1.6 x10^{-10} Acm^{-2}
ΔT= ±2.2 K
p= 7 $\mu Cm^{-2}K^{-1}$
θ = 94°



Pyroelectric current measurement for $Hf_{0.58}Zr_{0.42}O_2$ film.
J_{MAX}= 7.6 x10^{-10} Acm^{-2}
ΔT= ±2.8 K
p= 14 $\mu Cm^{-2}K^{-1}$
θ = 96°

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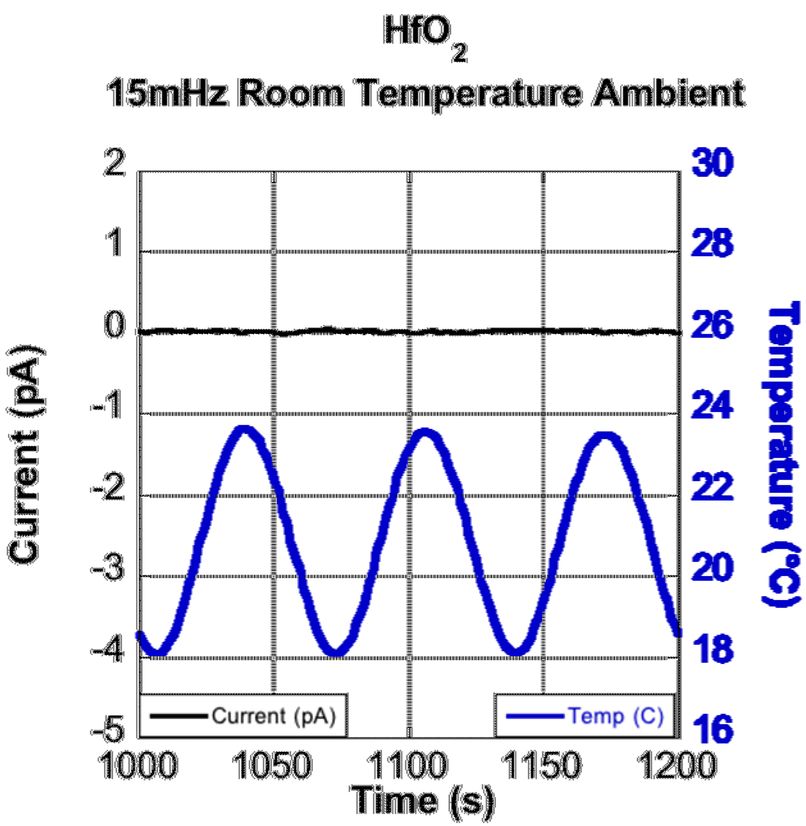
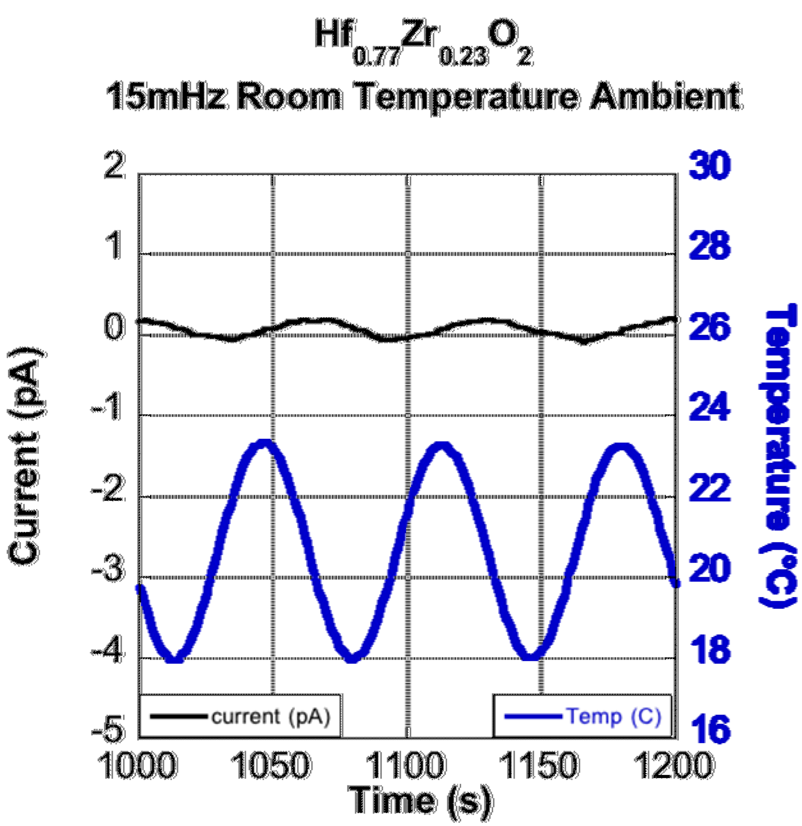
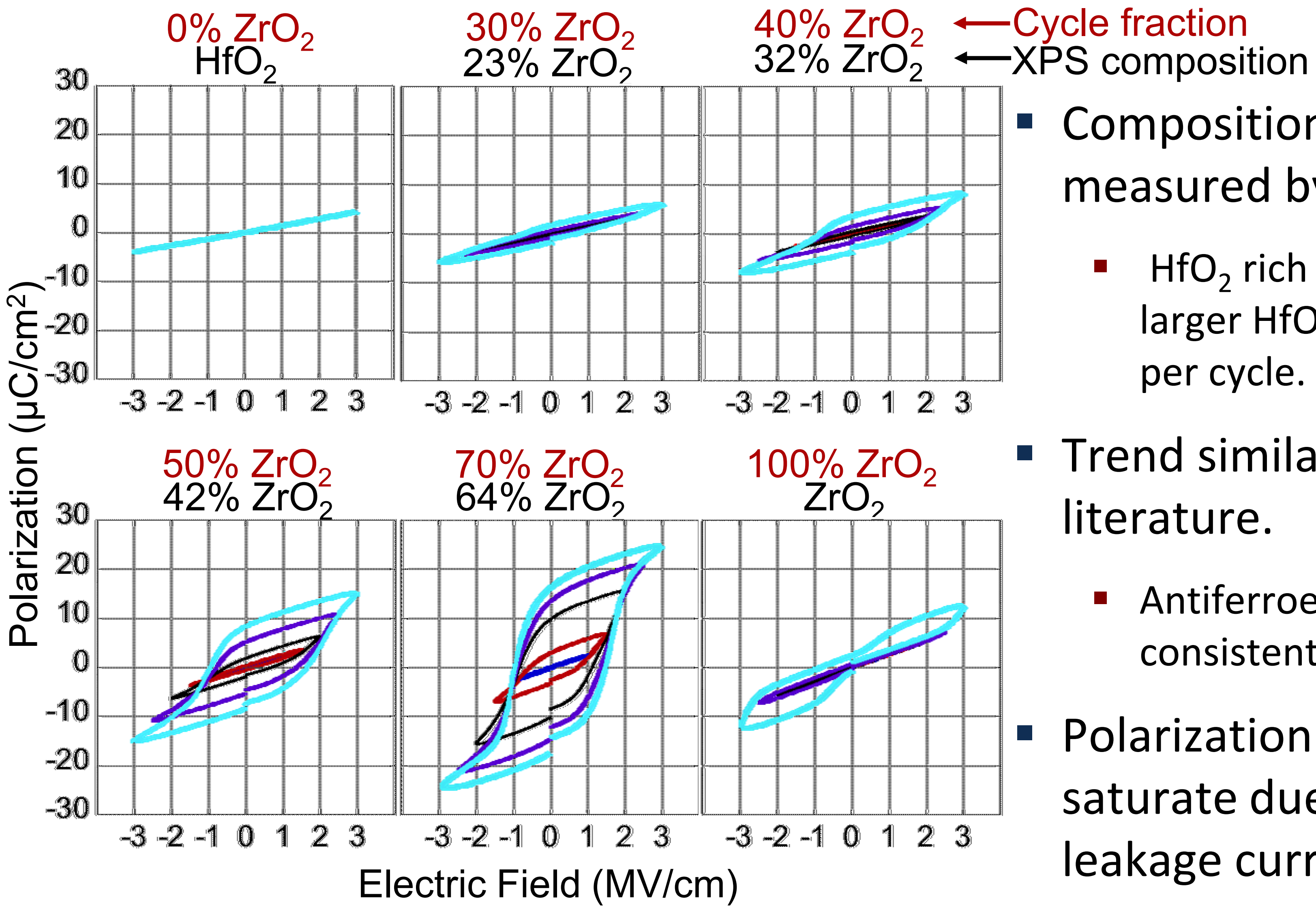


Pyroelectric current measurement for HfO_2 film.
J_{MAX}= 3.6 x10^{-11} Acm^{-2}
ΔT= ±2.8 K
p= NA



Pyroelectric current measurement for $Hf_{0.23}Zr_{0.77}O_2$ film.
J_{MAX}= 1.43 x10^{-10} Acm^{-2}
ΔT= ±2.8 K
p= 4 μCm^{-2}K^{-1}
θ = 98°

Polarization Electric Field Loops



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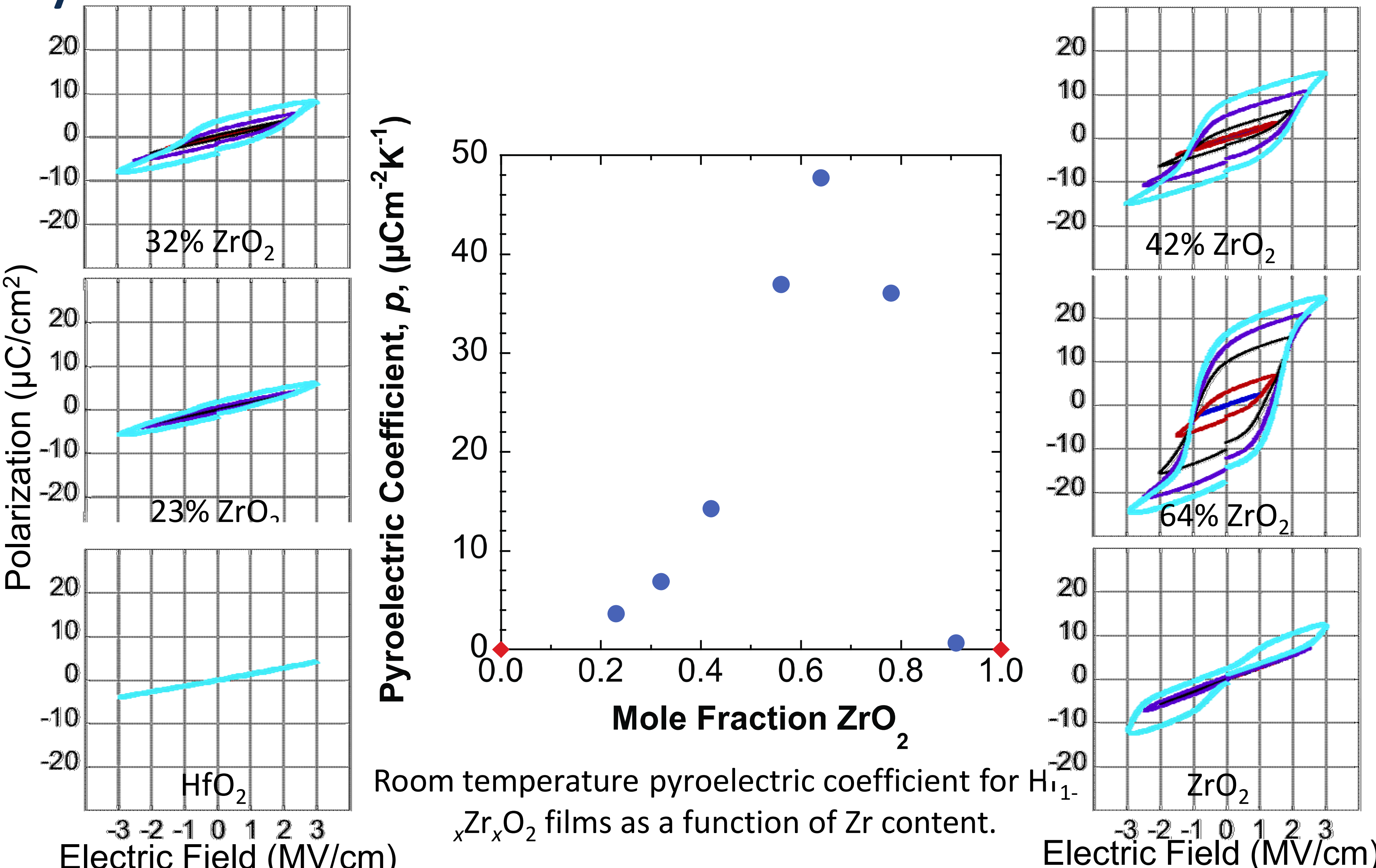

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