

Pyroelectric Response in $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ 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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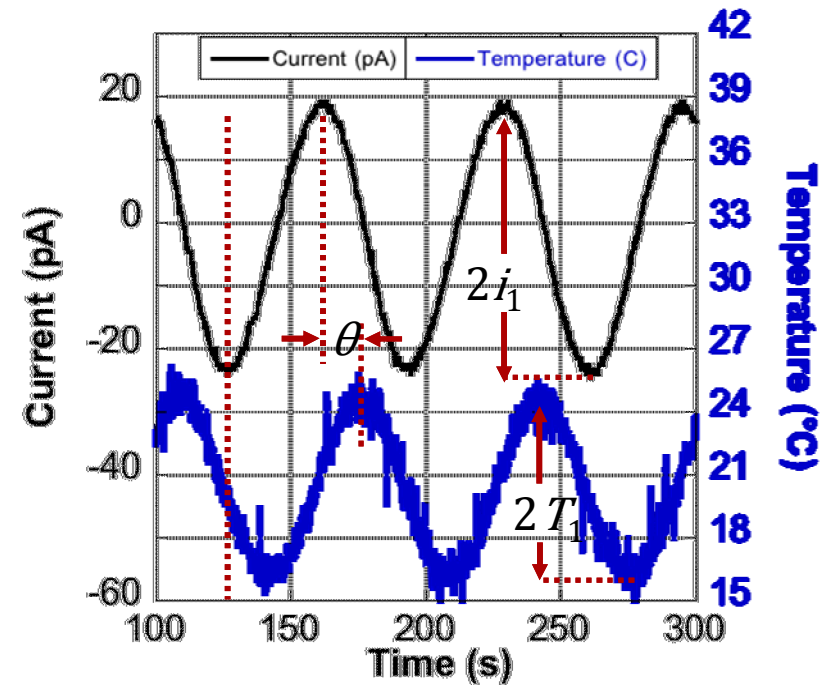
Doped HfO₂ Pyroelectric Response

- Ferroelectric with permanent polarization must have a pyroelectric response
- Park *et al.* Nano Energy 2014
 - Antiferroelectric Zr rich Hf_{1-x}Zr_xO₂ ($0.7 \leq X \leq 0.9$)
 - Measured Polarization-Electric field hysteresis curves at various Temperatures
- Hoffman *et al.* Nano Energy 2015
 - Si:HfO₂
 - Measured pyroelectric current with linear temperature ramp
- These methods can be influenced by extrinsic artifacts such as leakage current.

Pyroelectric Measurements

PLZT 4-20-80

15mHz Room Temperature Ambient



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

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

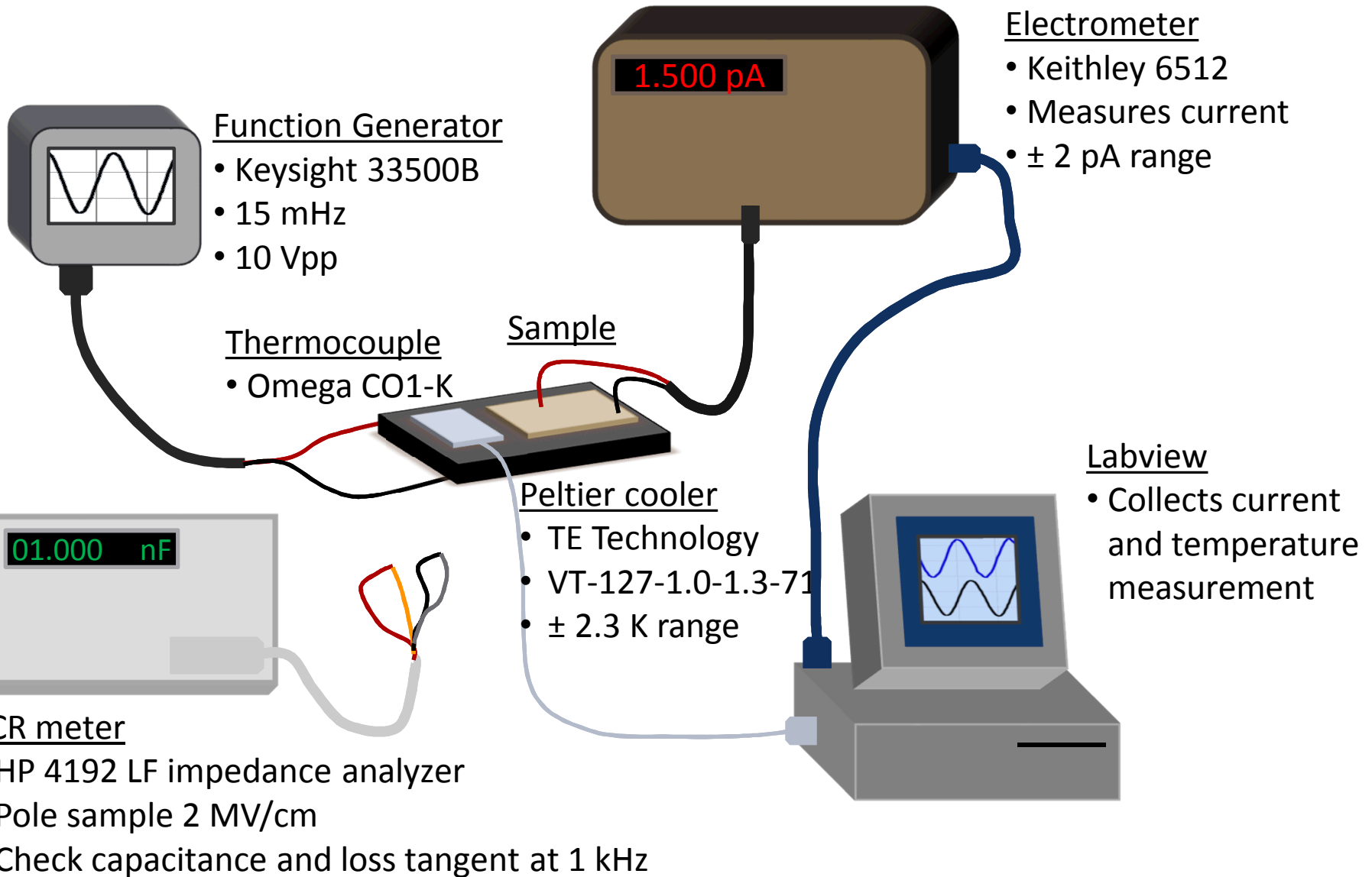
■ Static/Indirect

- Static: Discrete temperatures
 - Charge compensation by leakage current
- Indirect: Measure another physical parameter *i.e.* polarization
 - Incomplete switching or fatigue

■ Dynamic

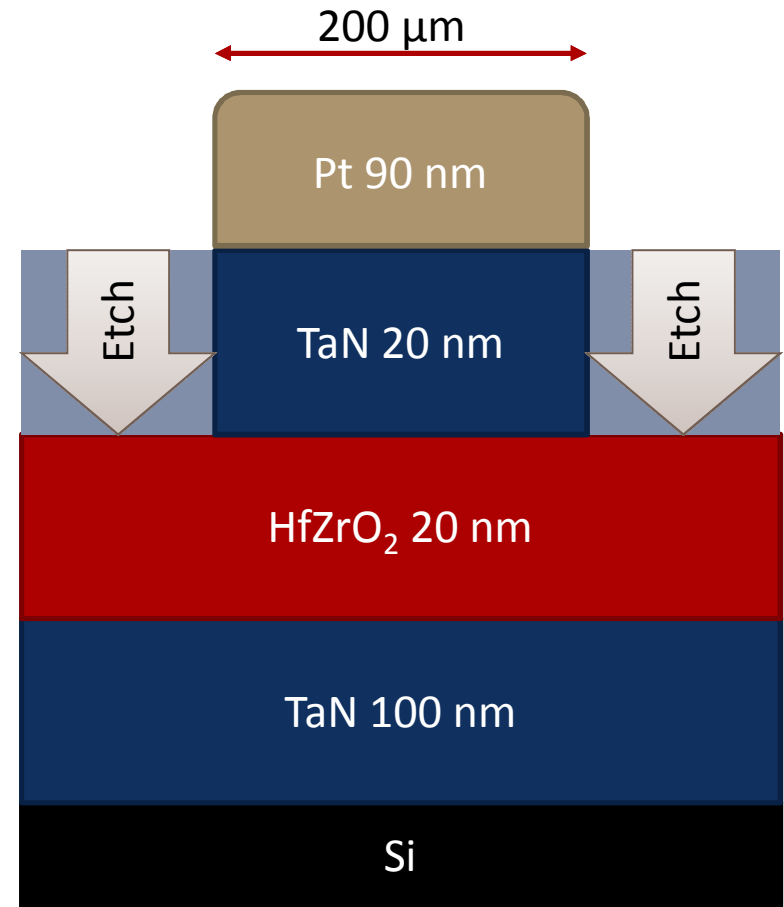
- Continuous change in temp and measure of current
- Linear temperature – (Byer-Roundy)
 - Difficult to separate pyroelectric and other thermally induced currents
- Oscillating temperature
 - Pyroelectric current depends on change in temperature with time

Pyroelectric Setup

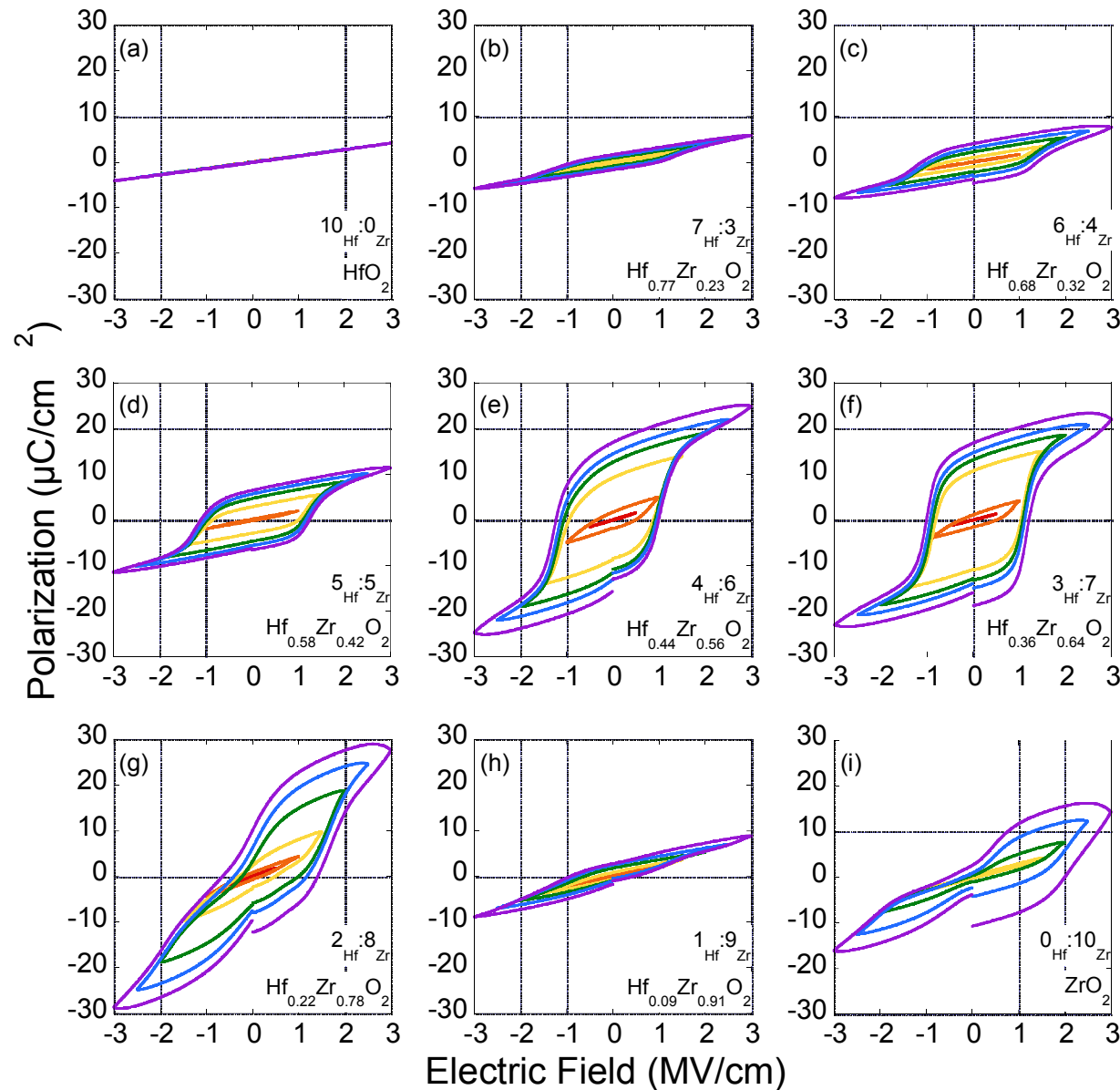


Experimental and Device Stack

- RF sputter TaN from TaN target
- Thermal ALD $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ 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



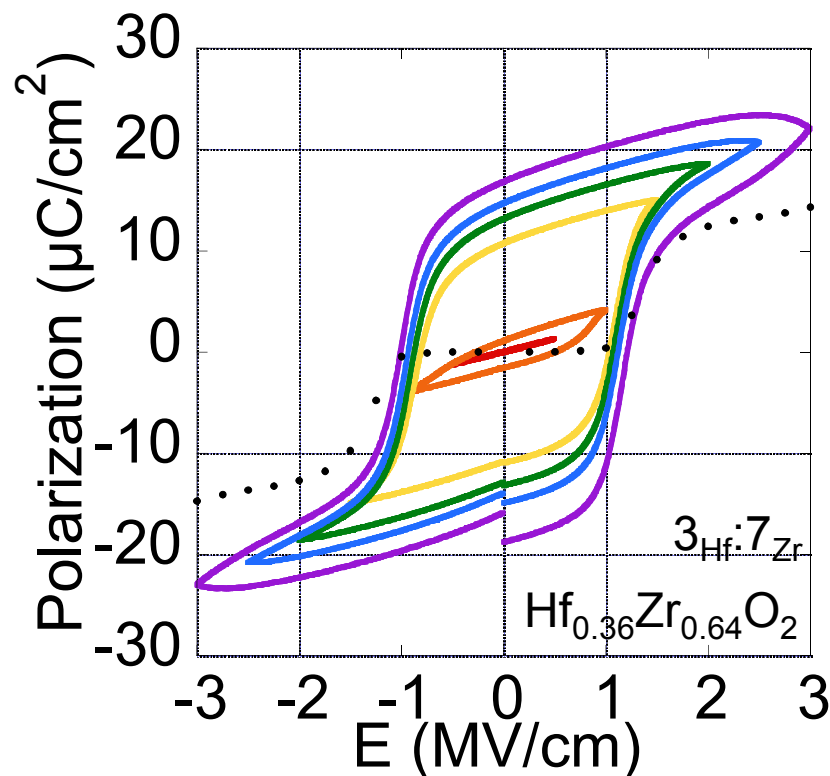
Polarization Electric Field Loops



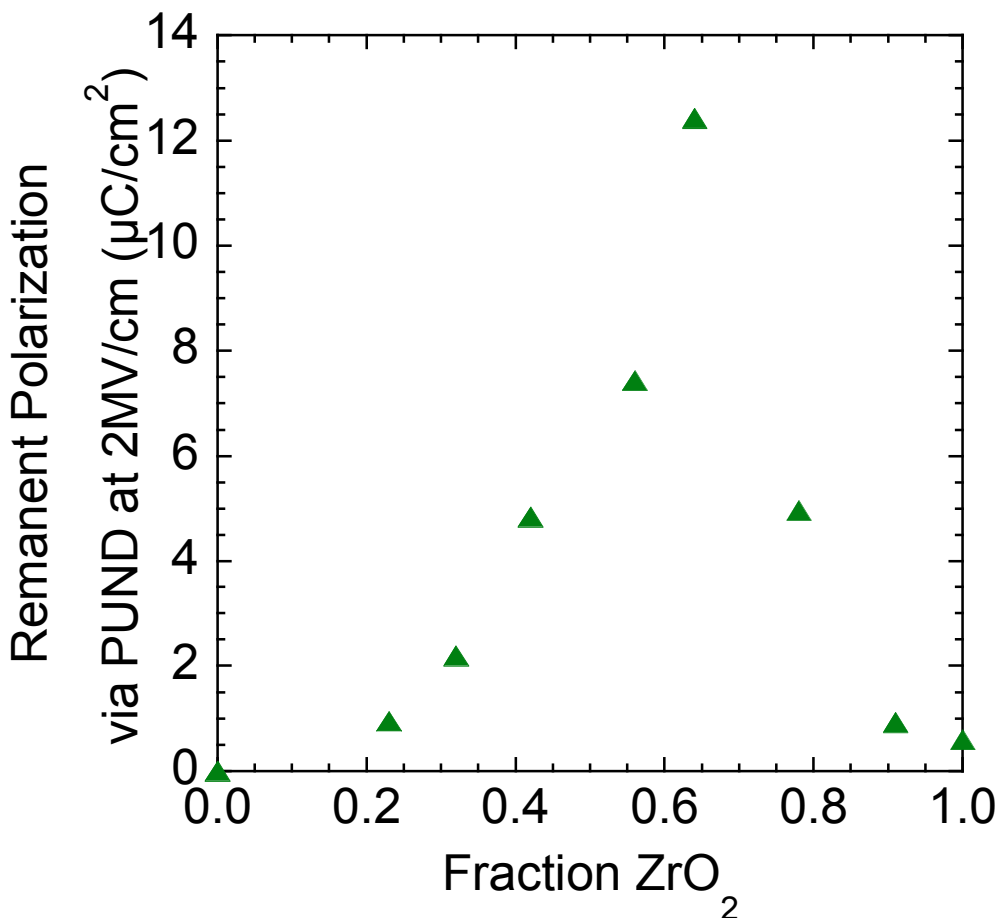
- Composition measured by XPS
 - HfO₂ rich due to larger HfO₂ growth per cycle
- 100 Hz measurement frequency
- Trend similar to literature
 - Antiferroelectric consistent with ZrO₂
- Polarization does not always saturate due to leakage current

Pulsed Positive Up Negative Down

- Finite leakage current contribution
 - 3 MV/cm across 20 nm films
- PUND Remanent Polarization
 - To measure P_r in ferroelectric memory
 - Doesn't saturate with $E \rightarrow$ wake up effect

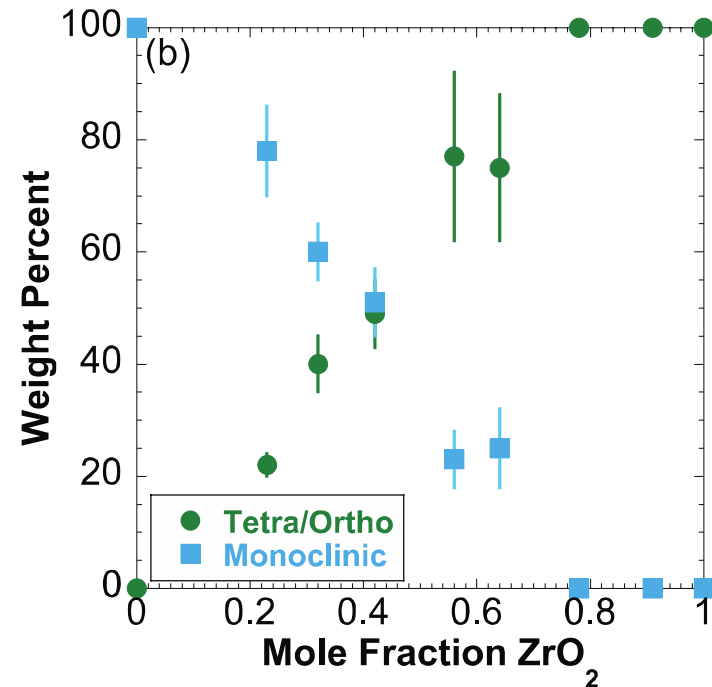
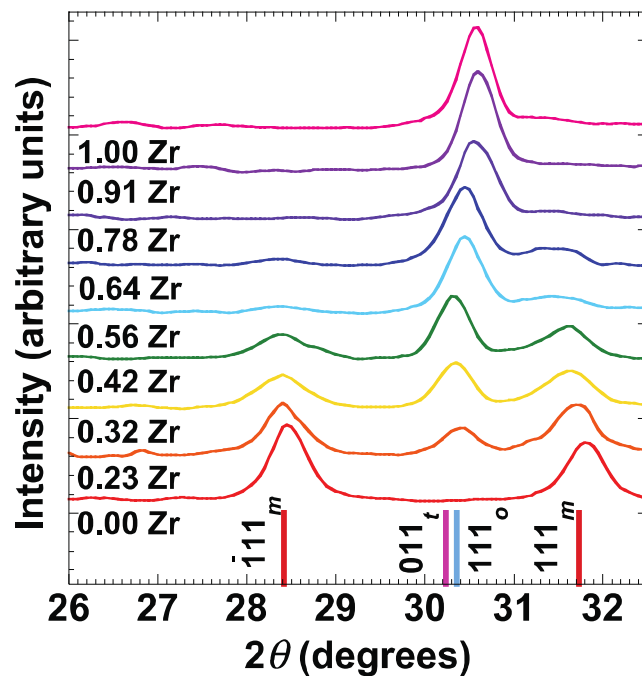


Pulsed Positive Up Negative Down



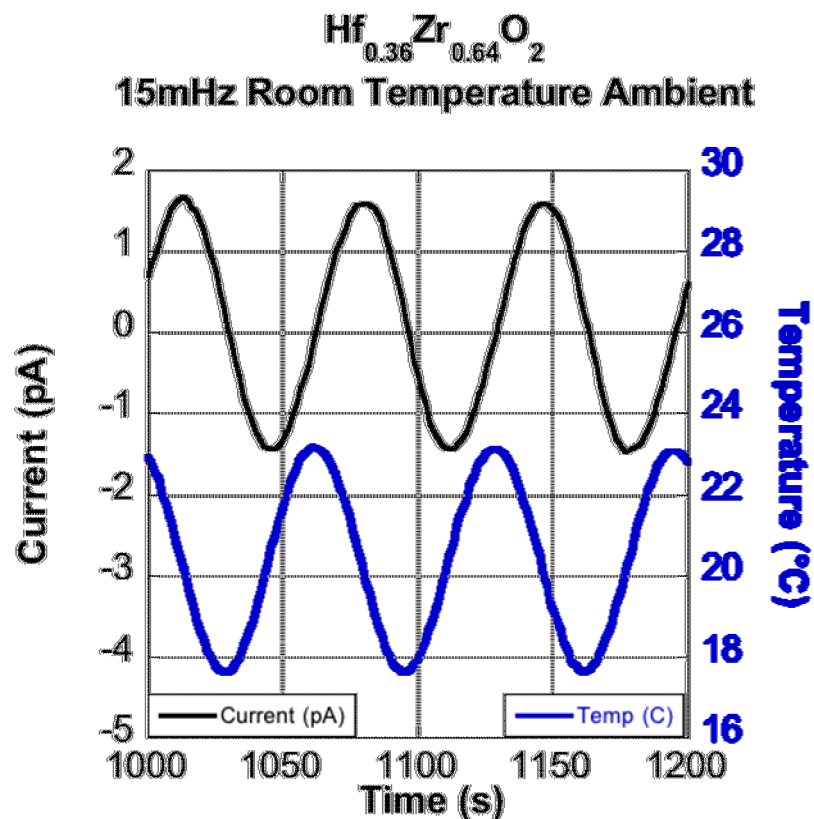
- Remanent polarization at 2 MV/cm via PUND
- Follows similar trend to PE loops
- Increasing P_r with fraction ZrO_2 up to 0.64

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

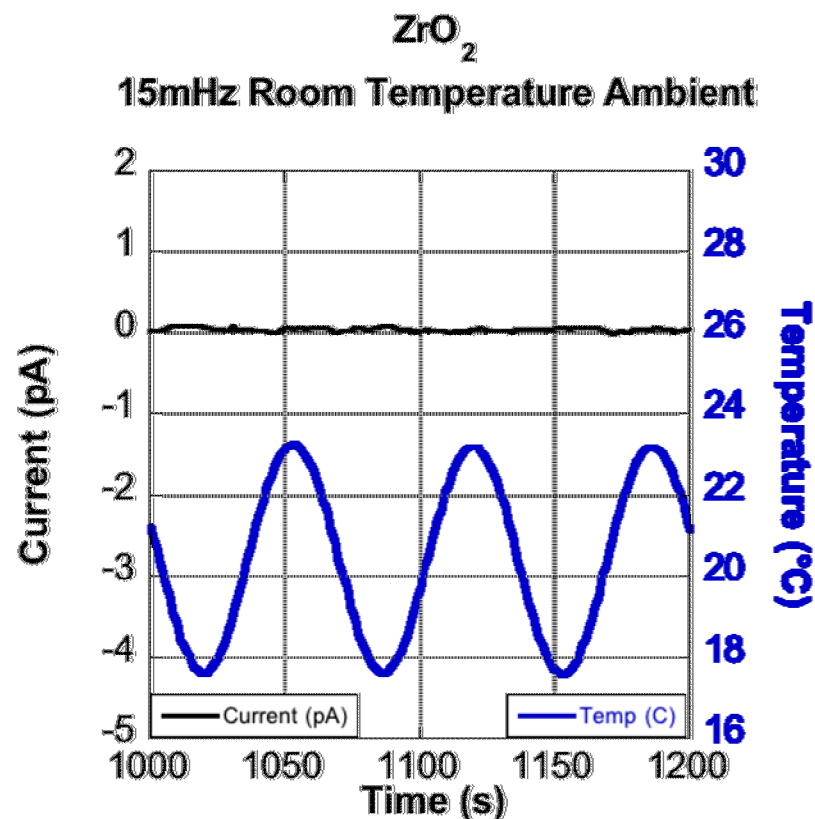
$\text{Hf}_{0.36}\text{Zr}_{0.64}\text{O}_2$ film.

$J_{\text{MAX}} = 1.33 \times 10^{-9} \text{ Acm}^{-2}$

$\Delta T = \pm 2.8 \text{ K}$

$\rho = 48 \mu\text{Cm}^{-2}\text{K}^{-1}$

$\theta = 94^\circ$



Pyroelectric current measurement for

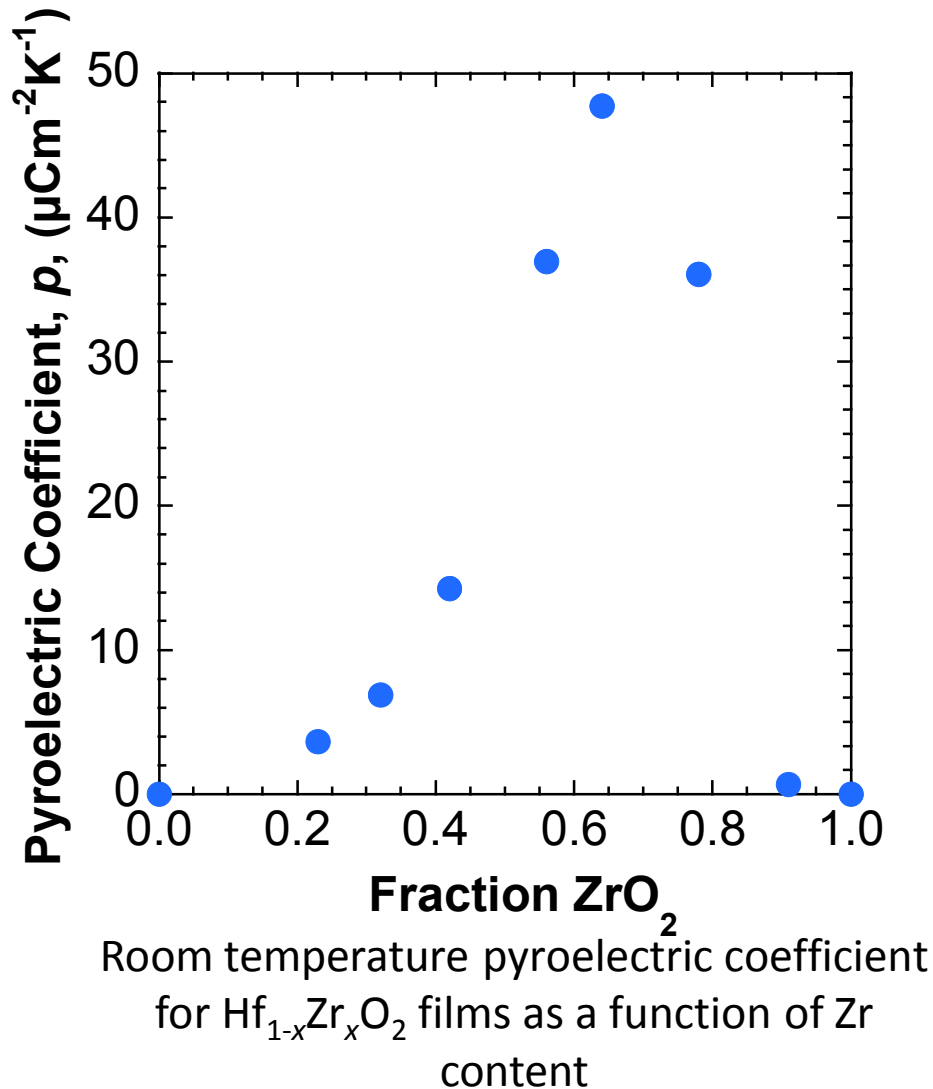
ZrO_2 film.

$J_{\text{MAX}} = 6.2 \times 10^{-11} \text{ Acm}^{-2}$

$\Delta T = \pm 2.9 \text{ K}$

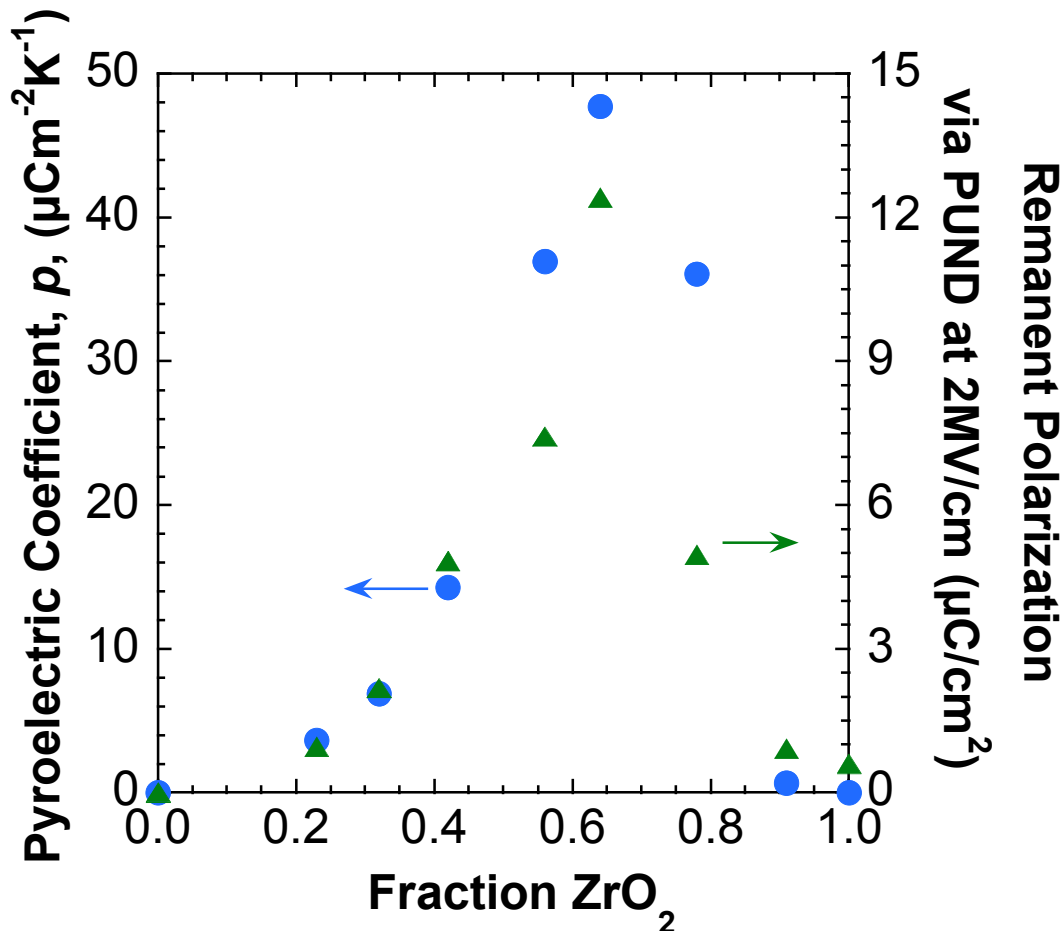
$\rho = \text{NA}$

Pyroelectric Coefficients



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

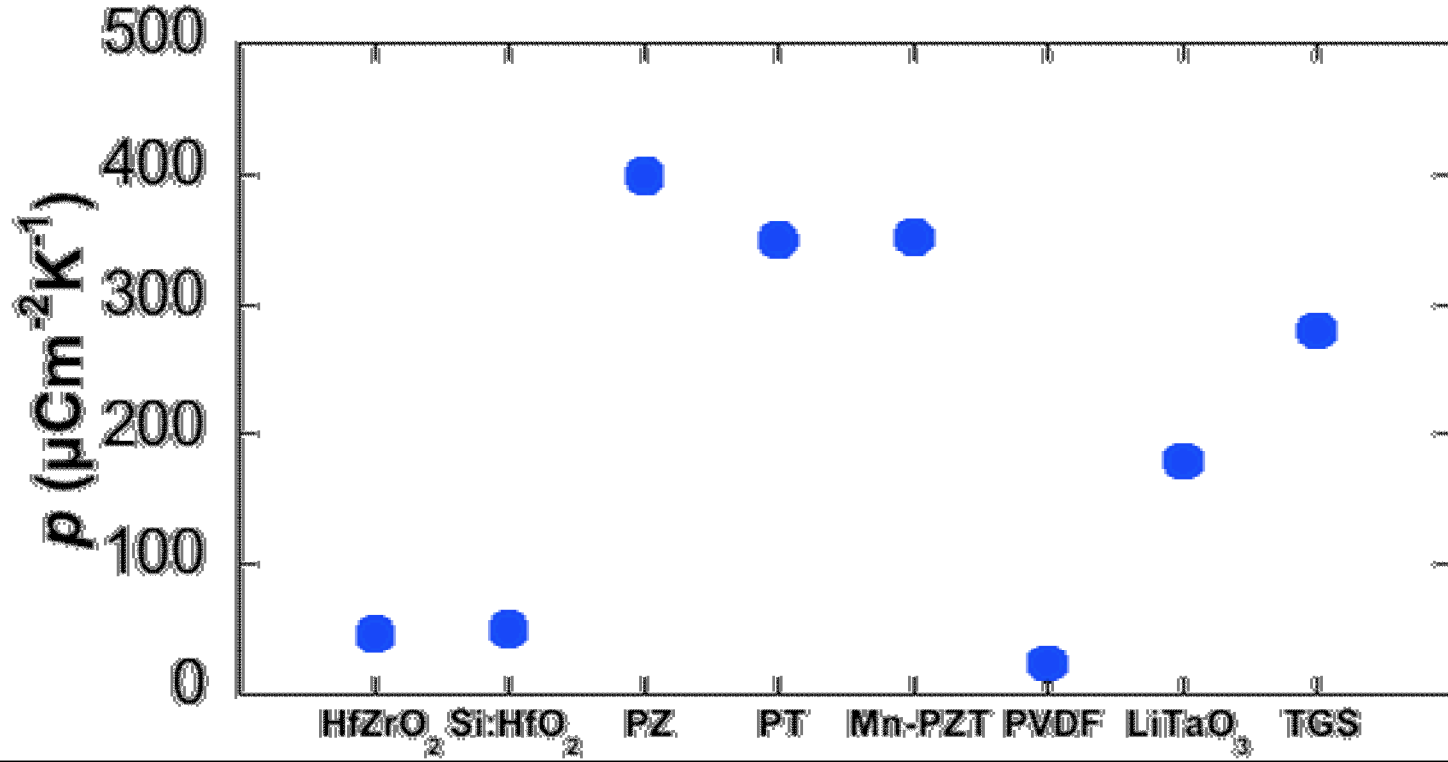
Pyroelectric Coefficients



Room temperature pyroelectric coefficient and P_r (2 MV/cm) for $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ films as a function of Zr content

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

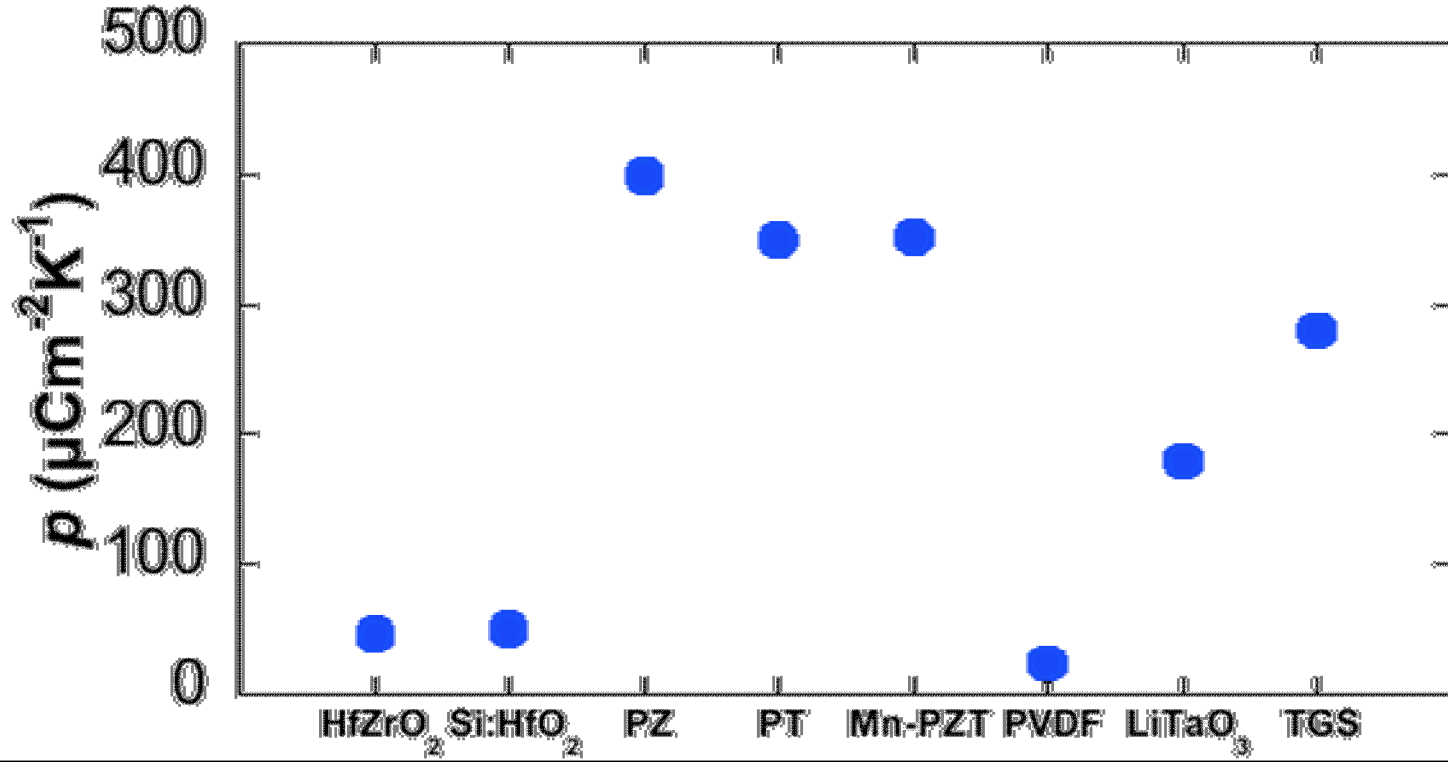
Hf_xZr_{1-x}O₂ & Other Materials



Material	p ($\mu\text{Cm}^{-2}\text{K}^{-1}$)	Dielectric properties		F_I 10^{-10} (mV^{-1})	F_V (m^2C^{-1})	F_D 10^{-6} ($\text{Pa}^{-1/2}$)	Reference
		ϵ_R	$\tan \delta$				
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 <i>Nano Energy</i>
Mod. PZ	400	290	0.003	0.02	0.06	58	Whatmore 2004 <i>J Electroceramics</i>
Mod. PT	350	220	0.01	0.01	0.07	32	
Mn -PZT thin film	352	257	0.007	-	-	39	Sebald 2008 <i>IEEE Trans.</i>
PVDF	25	9	0.03	0.11	0.14	7	Ploss 1991 <i>Sensors and Actuators A</i>
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}O₂ & Other Materials



Material	p ($\mu\text{Cm}^{-2}\text{K}^{-1}$)	Dielectric properties		F_I 10 ⁻¹⁰ (mV ⁻¹)	F_V (m ² C ⁻¹)	F_D 10 ⁻⁶ (Pa ^{-1/2})	Reference
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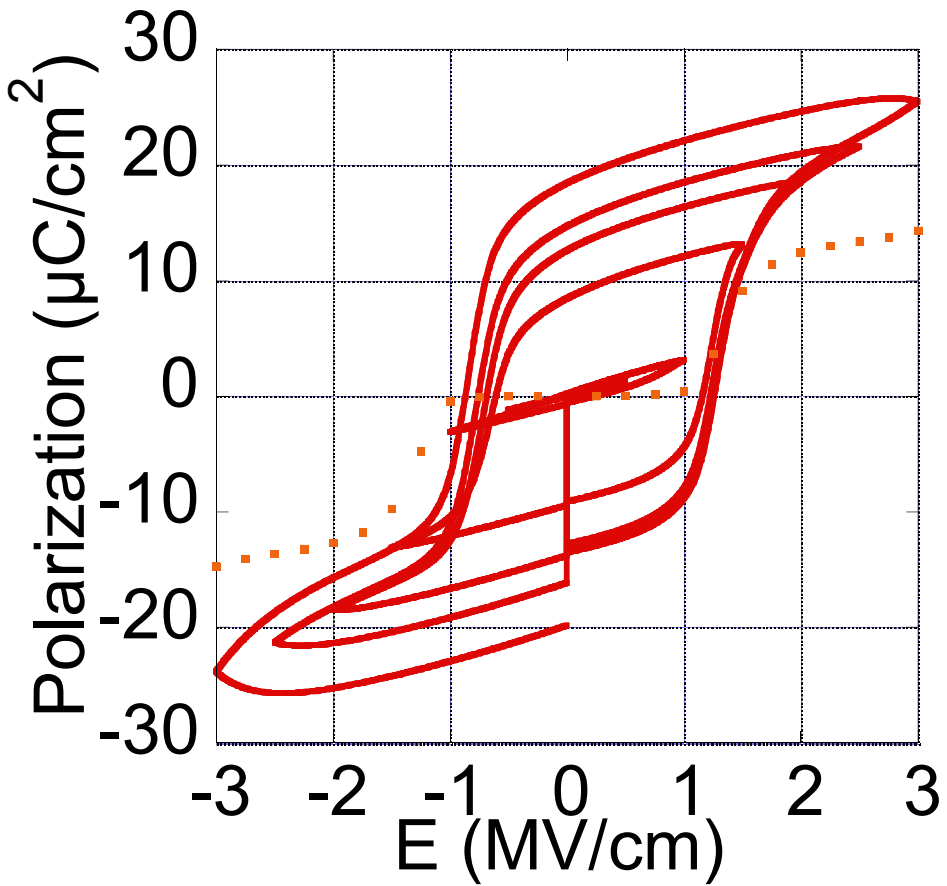
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Conclusions

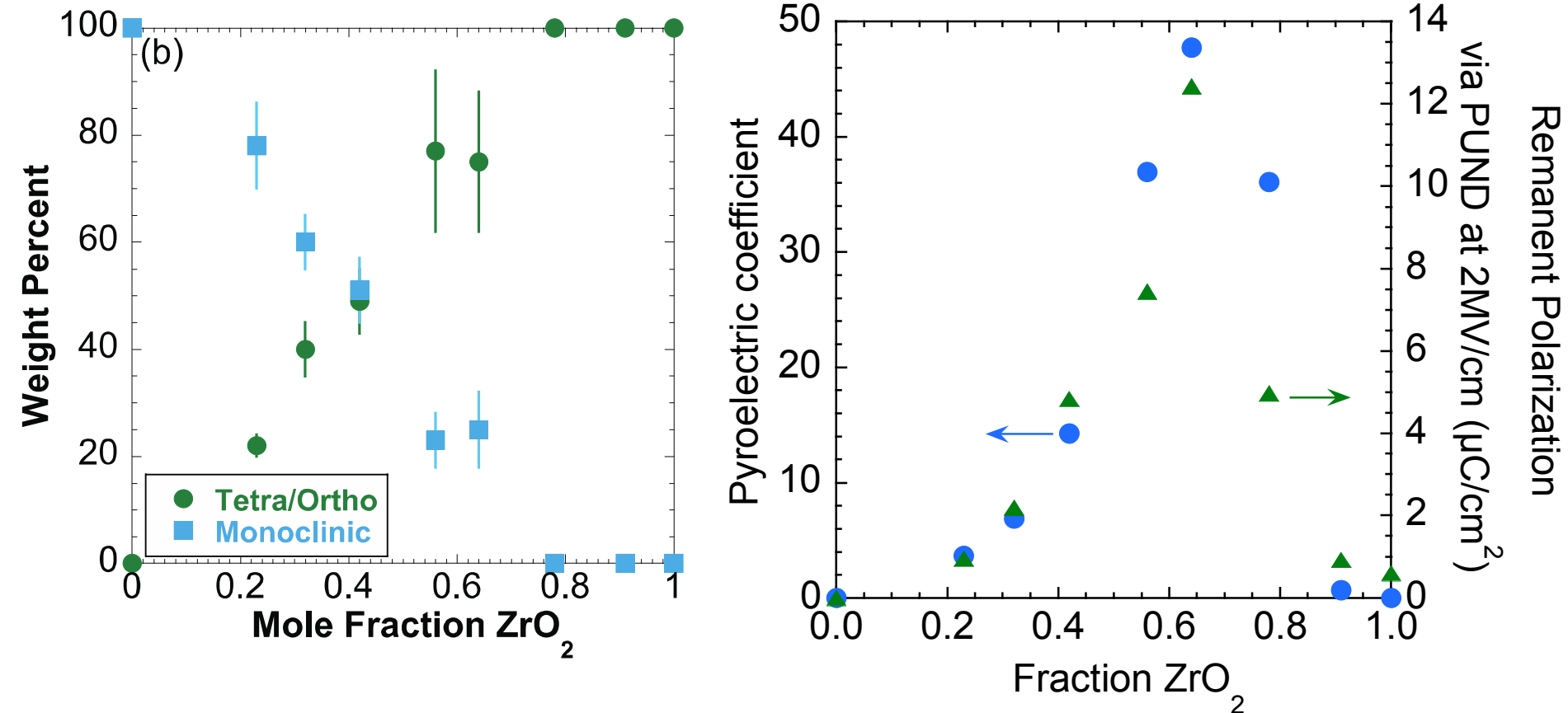
- We do observe a pyroelectric response in $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$
 - Consistent with permanent polarization
 - Consistent with ferroelectricity
- Pyroelectric response, remanent polarization, orthorhombic/tetragonal phase intensity, are all correlated with composition
- $\text{Hf}_{0.36}\text{Zr}_{0.64}\text{O}_2$ pyroelectric coefficient and IR detector figures of merit similar to PVDF and LiTaO_3
 - $p=48 \mu\text{Cm}^{-2}\text{K}^{-1}$
 - $F_I= 0.22 \text{ mV}^{-1}$
 - $F_V= 0.10 \text{ m}^2\text{C}^{-1}$
- This could be a promising material for large area IR detectors or low frequency detection

BONUS SLIDES

PUND

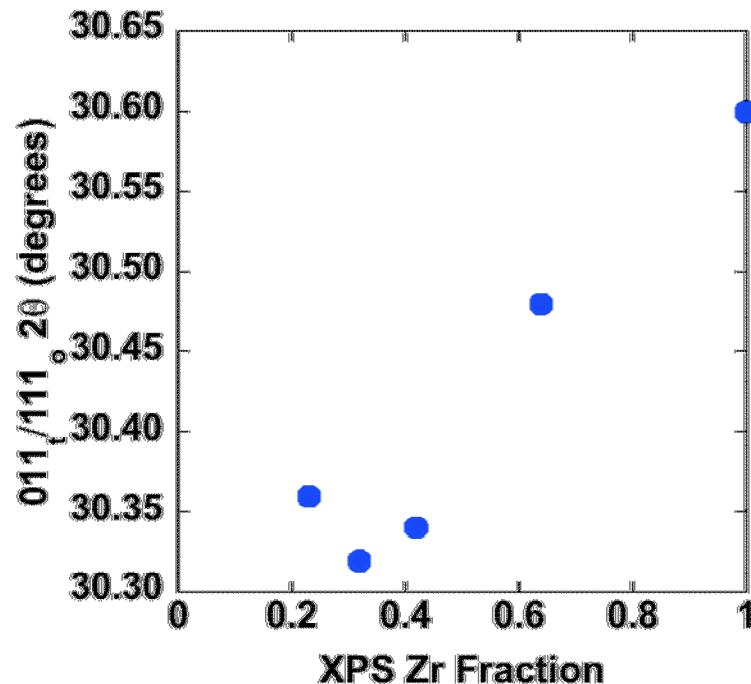
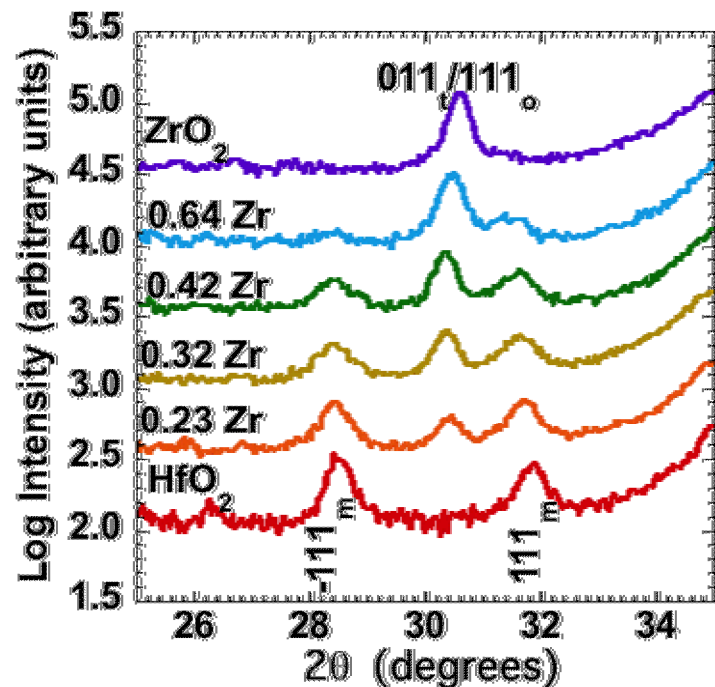


Pyroelectric Coefficients



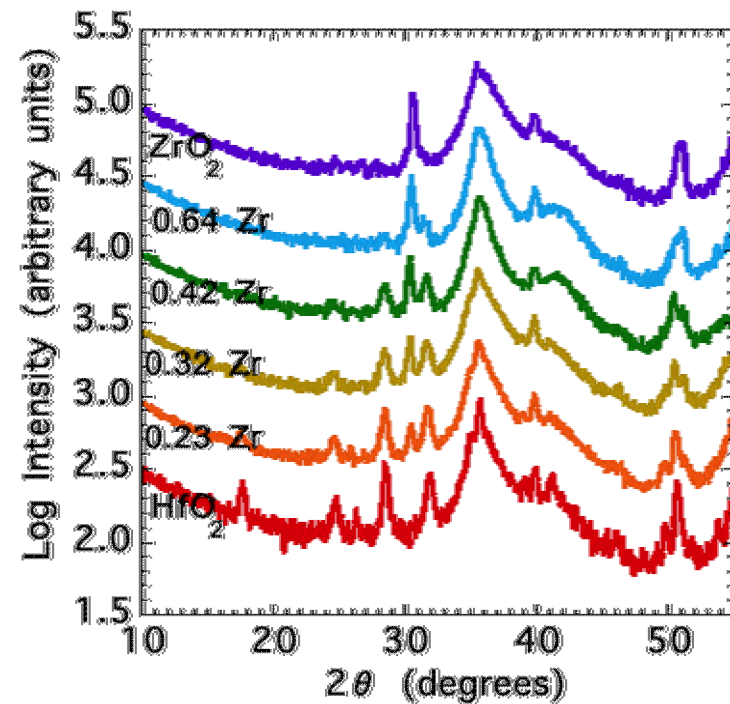
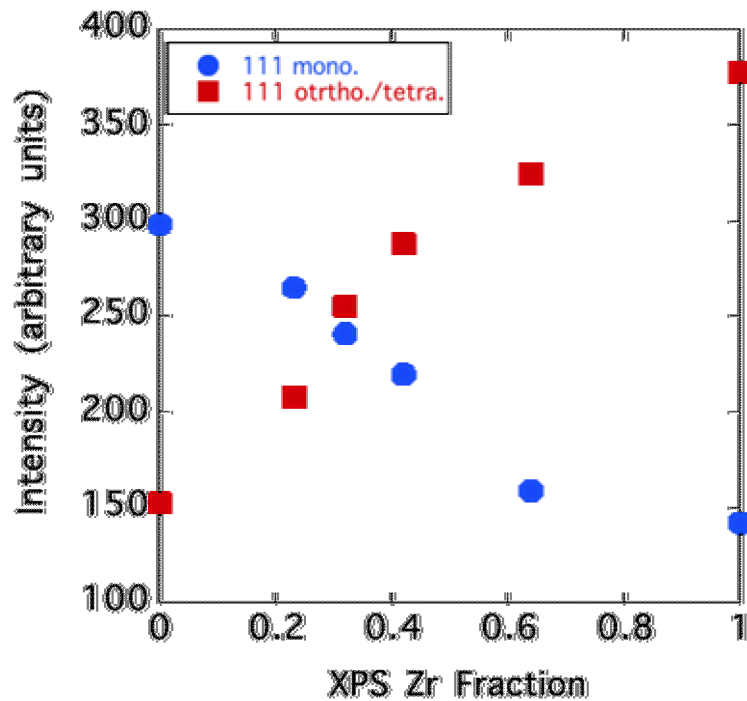
Room temperature pyroelectric coefficient and PUND measured remanent polarization at 2 MV/cm for $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ films as a function of Zr content.

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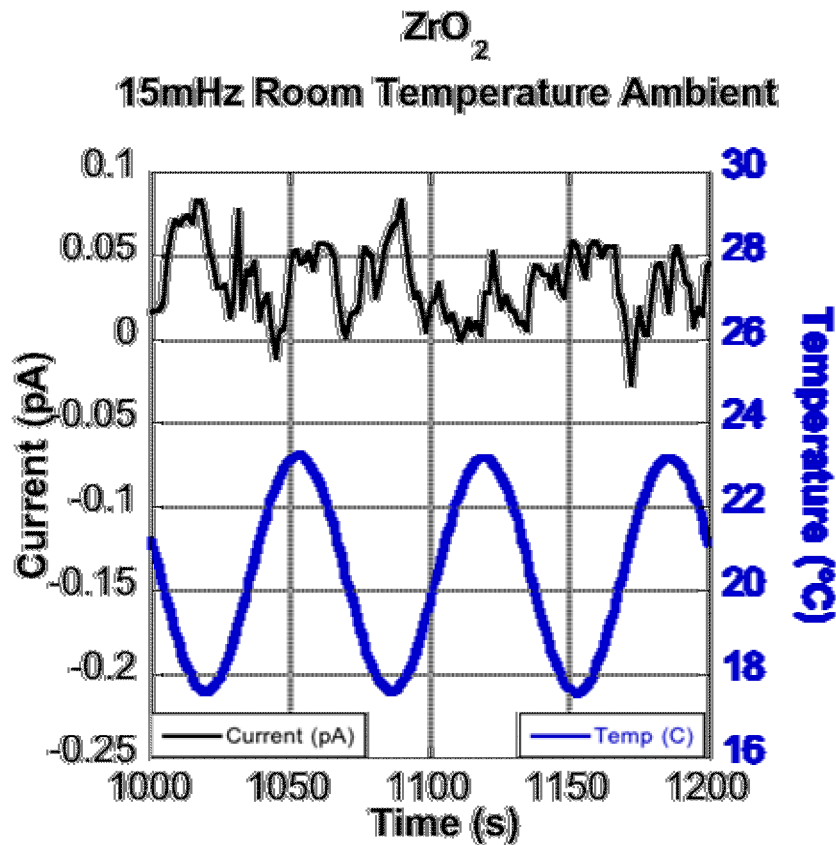


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X-ray results



ZrO₂ pyro waveforms zoomed in

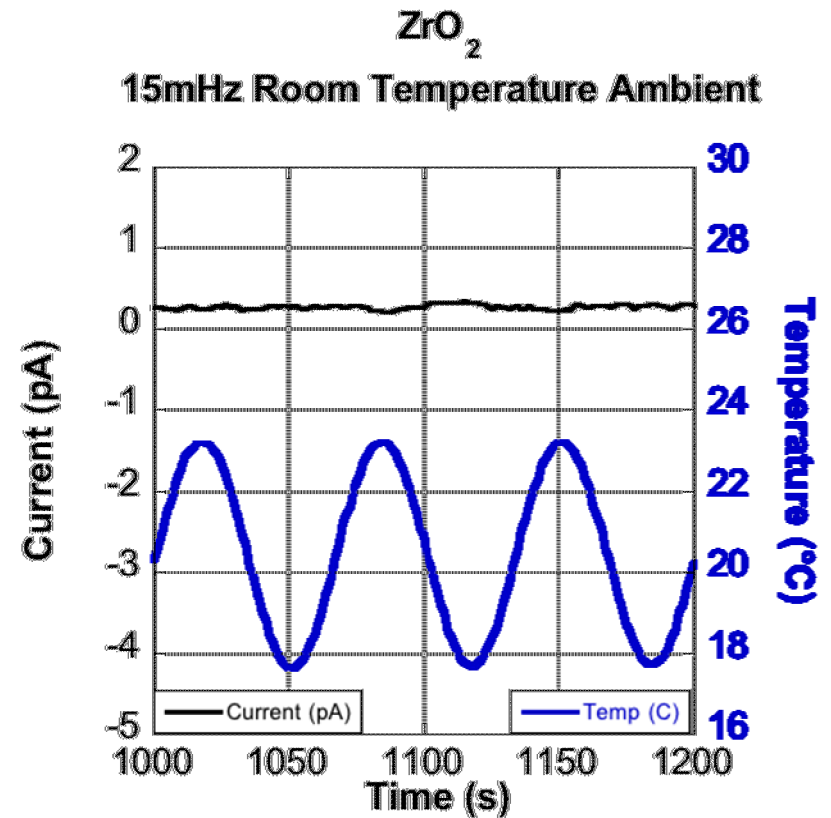


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