SAND2016-11767C

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Pyroelectricity in Atomic Layer Deposited $Hf_{1-x}Zr_xO_2$

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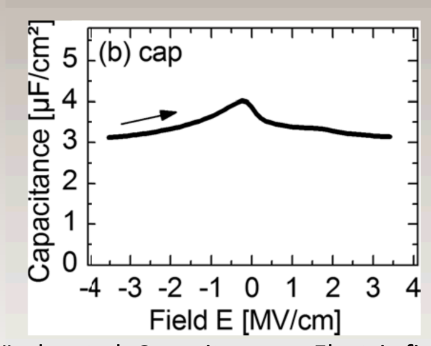
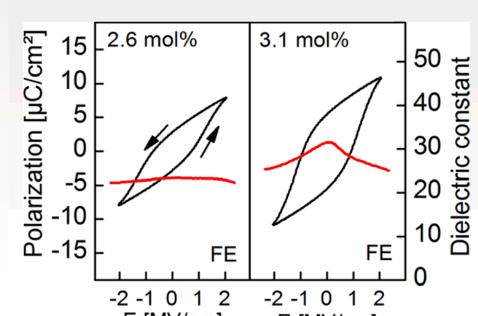
1. Introduction

- In 2011 Böscke et al. controversially recorded a ferroelectric like response in 2 to 5% Si:HfO_2 with TiN top and bottom electrodes.
- Similar results have since been reported for other HfO_2 based systems including $(Hf,Zr)O_2$
- Community skeptical
- To settle the debate: if ferroelectric then also pyroelectric.
- Two groups proposed pyroelectric coefficients but both used methods which can be influenced by extrinsic artifacts such as leakage current.
- Here we present rigorous pyroelectric measurements to establish ferroelectricity.



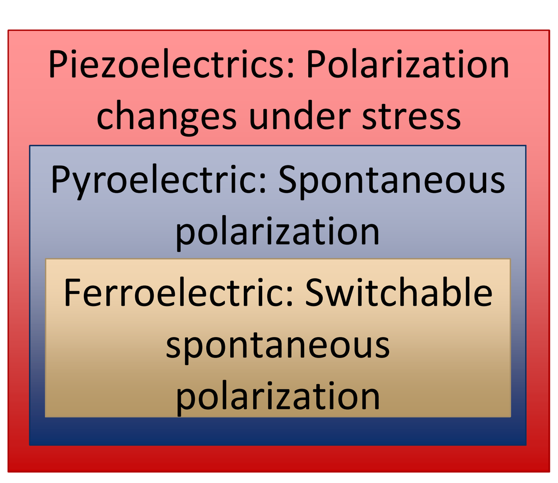
Böscke et al. Capacitance vs Electric field showing peak associated with polarization.

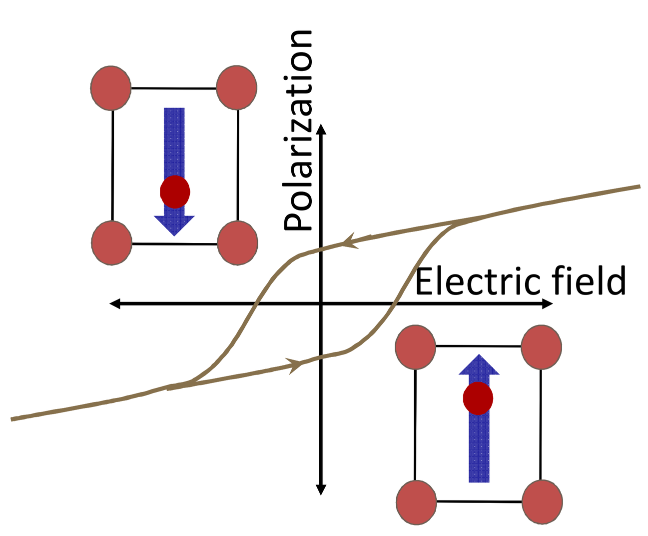


Böscke et al. Polarization (black) and dielectric constant (red) vs Electric field for 2 Si doping levels.

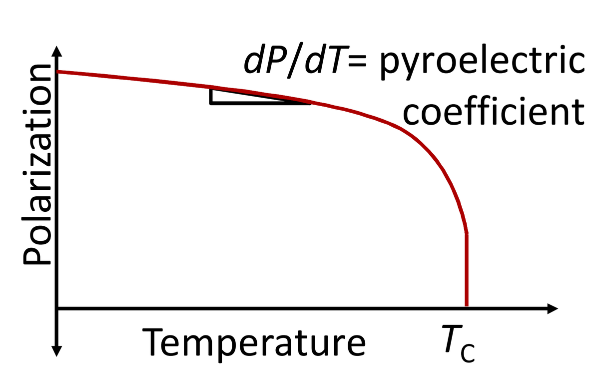
2. Pyroelectricity and Ferroelectricity

All ferroelectrics are also pyroelectric.





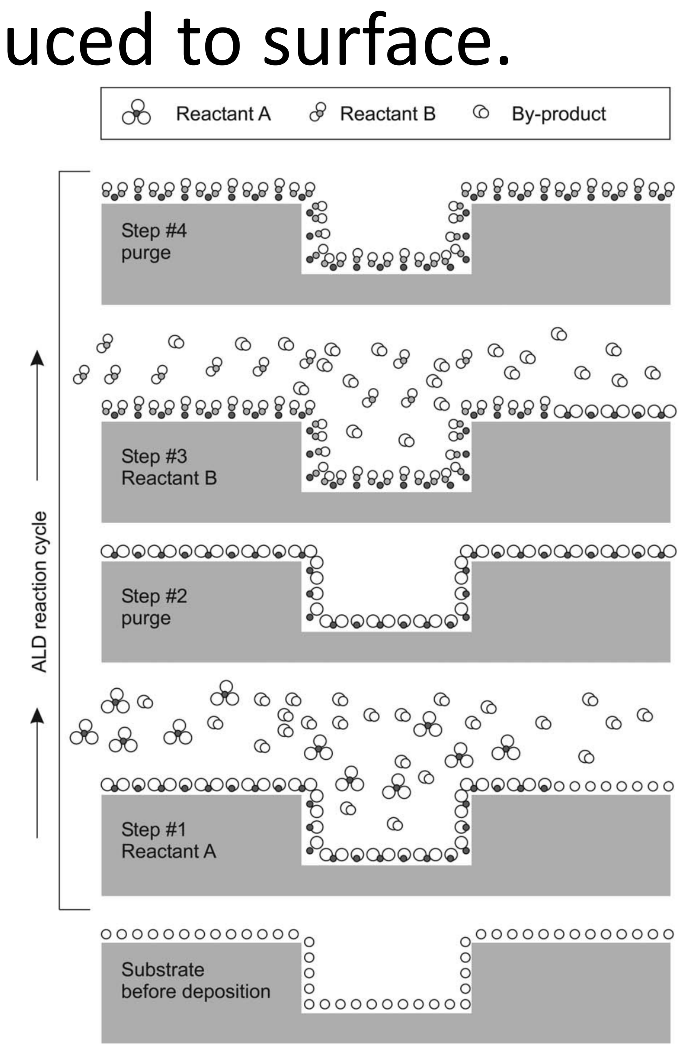
- Uniform change in temperature creates a change in polarization.
  - Must have spontaneous polarization.
  - With electrodes change in polarization can be measured as a voltage or current.



3. Atomic Layer Deposition

Gas phase deposition with reactants alternately introduced to surface.

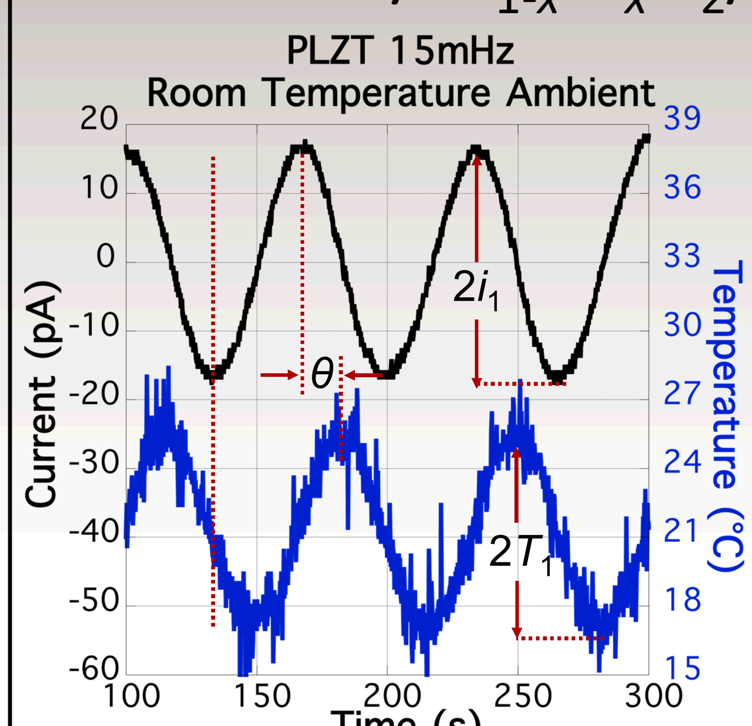
- Variant of chemical vapor deposition.
- Alternate doses of precursors separated by inert gas purge.
- Reaction limited to chemisorbed surface layer.
- Pinhole free films
- Precise thickness and composition control.
  - Sub monolayer growth per cycle.
- Multicomponent can be done by layering two or more systems.



Schematic of ALD process.
R. L. Puurunen, *J. Appl. Phys.* **97**, 121301 (2005)

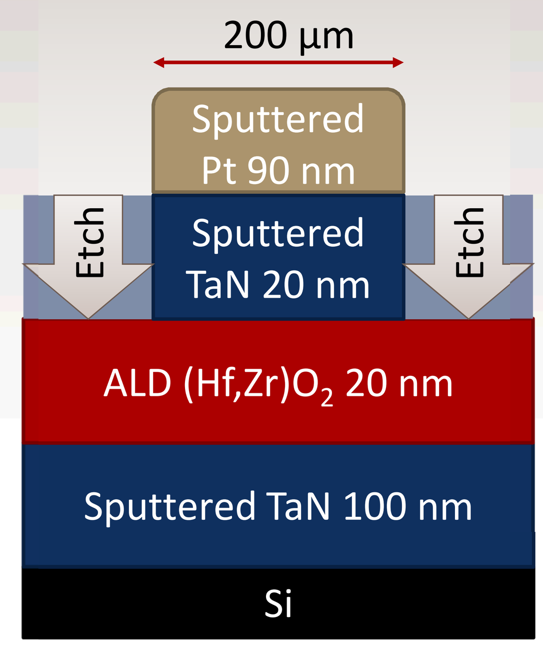
4. Experimental Procedure

TaN/$Hf_{1-x}Zr_xO_2$/TaN stack

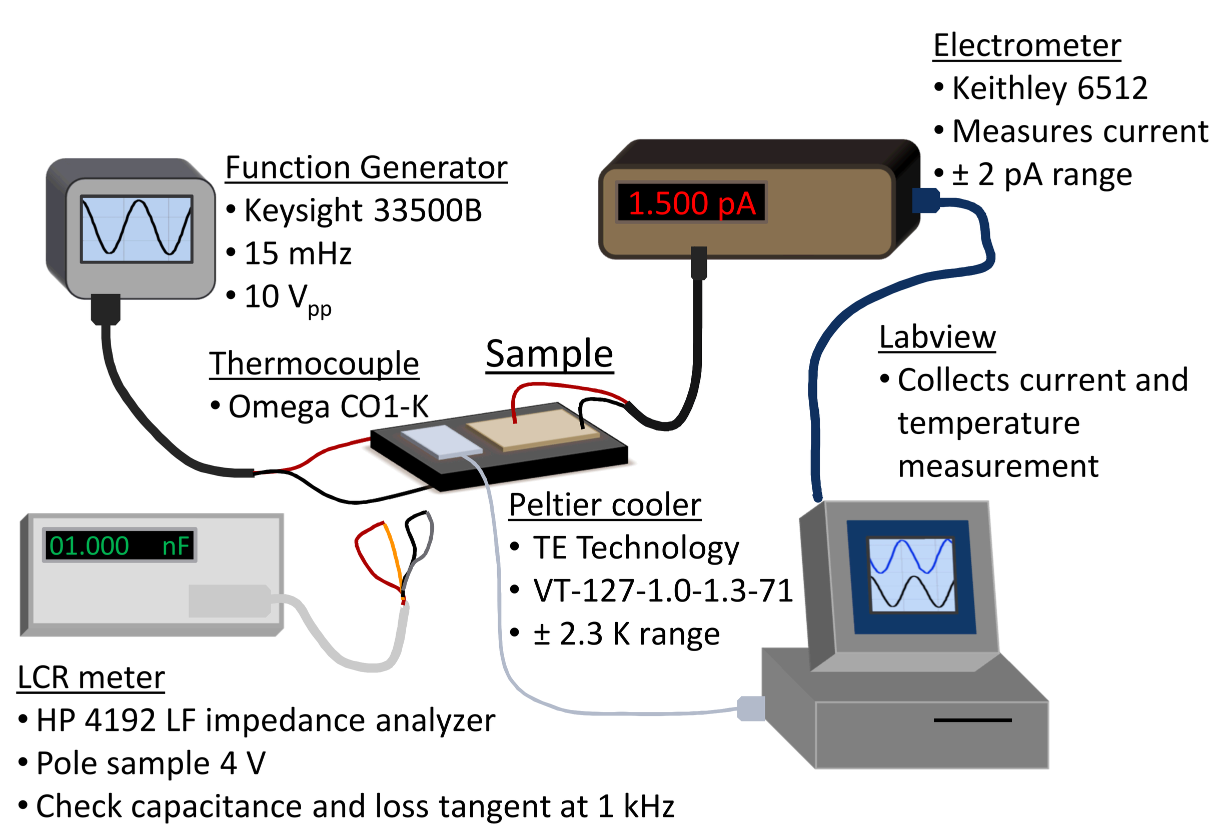


$$i_1 \sin(\theta) = pA\omega T_1$$

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

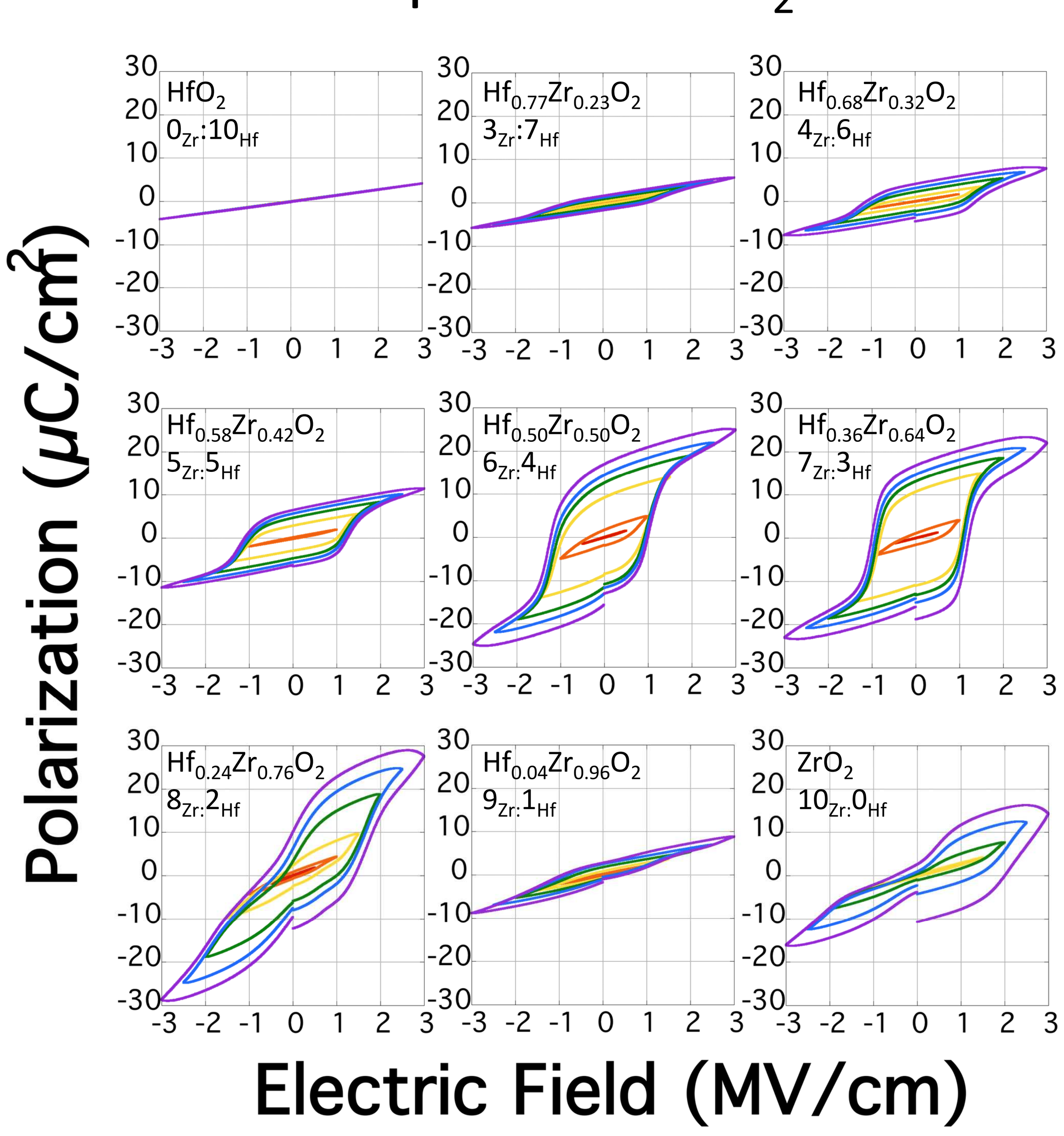


Device stack schematic



5. Polarization Response

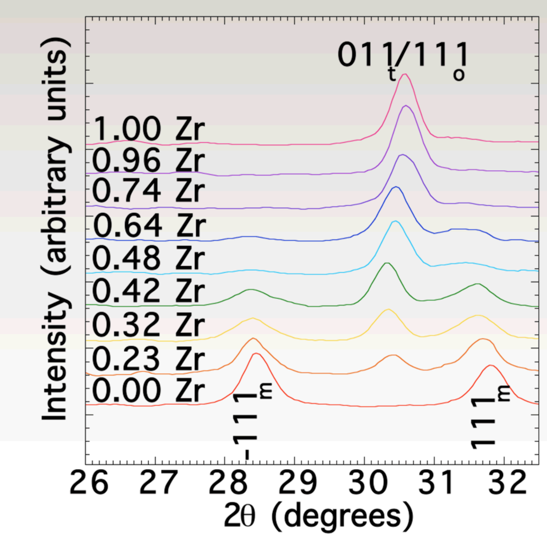
Remanent Polarization increases with Zr content up to 0.64 ZrO_2 fraction.



Polarization electric field data for composition array. XPS determined composition and ALD cycle ratio are listed.

6. Crystal Phase

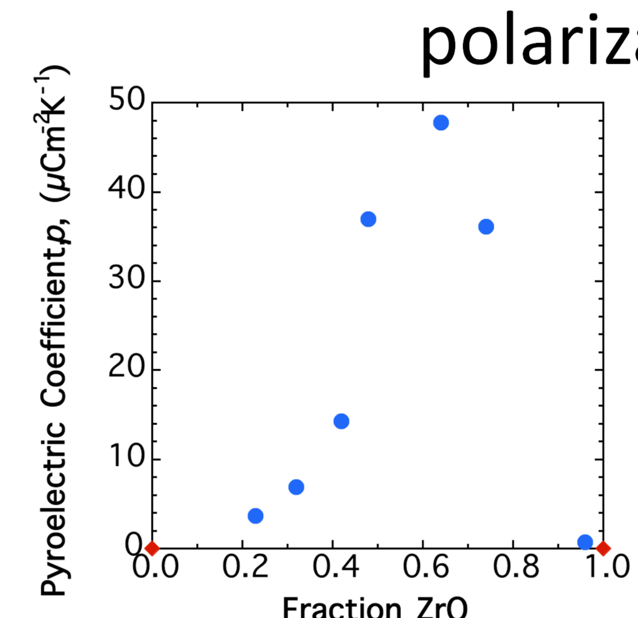
Orthorhombic/tetragonal phase fraction increases with ZrO_2 content.



- Orthorhombic phase associated with ferroelectricity response indistinguishable from tetragonal ZrO_2 phase.
- Decrease in monoclinic phase, corresponds with increase in Zr content and polarization.

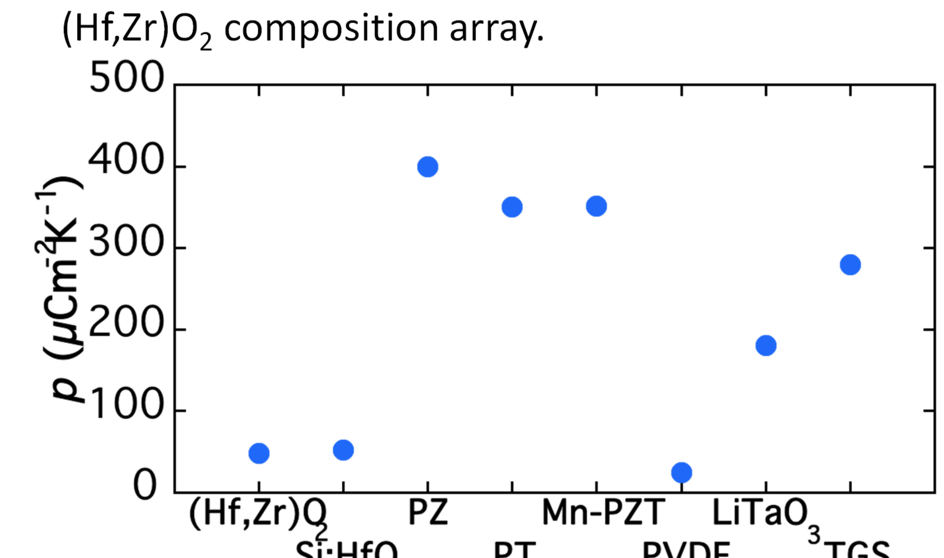
7. Pyroelectric Response

Pyroelectric response correlated with polarization.



Pyroelectric Coefficients for $(Hf,Zr)O_2$ composition array.

- Pyroelectric coefficients increases with ZrO_2 fraction up to 0.64.
- Correlated with polarization response.
- p lower than many ferroelectrics but lower dielectric constant makes infrared detector figures of merit comparable.



Pyroelectric Coefficient for $(Hf,Zr)O_2$, Si:HfO_2 and several common pyroelectrics.

Pyroelectric Coefficient, dielectric properties and infrared detector figures of merit for $(Hf,Zr)O_2$, Si:HfO_2 and several common pyroelectrics.

Material	p ($\mu Cm^{-2}K^{-1}$)	Dielectric properties ε_r	Dielectric properties tan δ	F_I 10^{-10} (mV^{-1})	F_V (m^2C^{-1})	F_D 10^{-6} ($Pa^{-1/2}$)	Reference
$Hf_{0.32}Zr_{0.64}O_2$	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	

8. Summary

- Observed pyroelectric response in $Hf_{1-x}Zr_xO_2$.
  - Consistent with permanent polarization.
  - **$(Hf,Zr)O_2$ is likely a ferroelectric material.**
- 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 $LiTaO_3$.
- $(Hf,Zr)O_2$ is a promising material for large area IR detectors or low frequency detection.

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NNSA National Nuclear Security Administration

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SAND2016-11235 A