SAND2011-9335 C
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$Ca(Zr,Ti)O_3$ Ceramics for Energy Storage Applications

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Sandia National Laboratories
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Outline

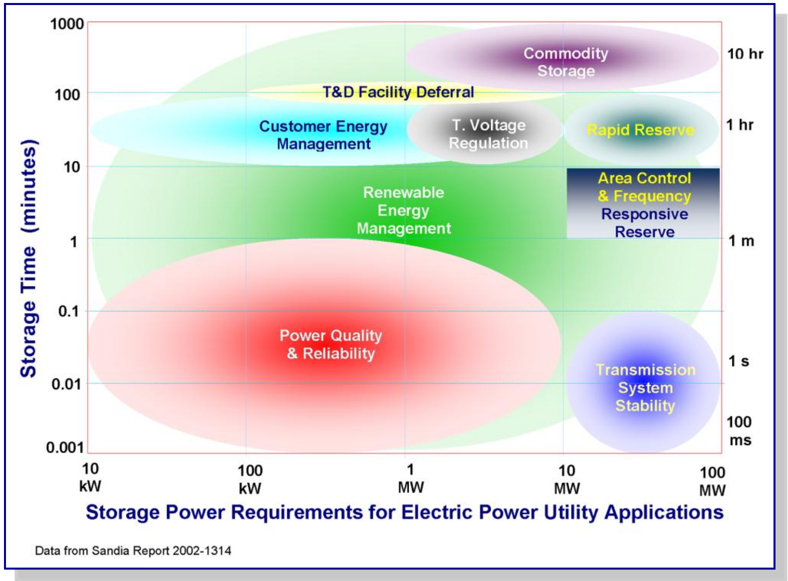
- Introduction
- Chemical powder synthesis route
  - $Ca(Zr_{0.9}Ti_{0.1})O_3 \rightarrow$ CZT90/10
- Fabrication of multilayer CZT
  - Powder calcination and 2-step sintering
  - Free standing single and multilayer CZT90/10
- Characterization
  - Microstructure
  - Dielectric properties
  - Energy density
- Summary

Application Requirement

- **Next-Generation Capacitor Requirements:**
  - **Reduced volume and temperature insensitive dielectric property**

- **Potential Applications:**
  - **Power Grid**
  - **Electric Hybrid and Fuel Cell Vehicles**
  - **High Frequency Applications**

- **Impact:**
  - **Increased system reliability**
  - **Smaller component packages**



Toyota Prius Inverter

The large capacitors ~ 35 Vol% of the inverter, the largest and most unreliable parts in the inverter

Trade-offs of Dielectric Materials

Properties	Low K, high E_{bd}, low TCC	Medium K, high E_{bd}, moderate TCC	High K, medium E_{bd}, high TCC
ε	30	80	1200
Tcc (ppm/°C)	120	1000	> 2000
$\Delta\varepsilon$ over 200 °C	2.4%	20%	30 – 50%
Example	$CaZrO_3 – CaTiO_3$	TiO_2	PLZT

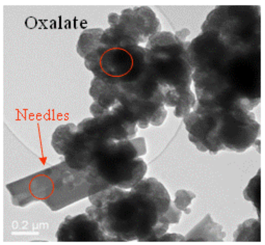
Focus of this presentation

ε: dielectric constant
E_{bd}: dielectric break down field
T_{cc}: temperature coef of capacitance

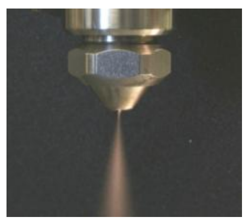
Material and Process Review

Previous work on $CaZrO_3$

Synthesized powder

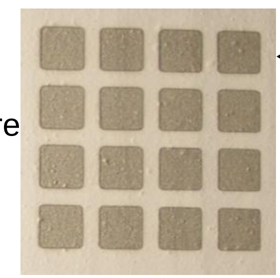


Solution chemistry



Aerosol spray deposition

Test structure



SNL CZ Thick Films (50 µm)

measured under identical conditions

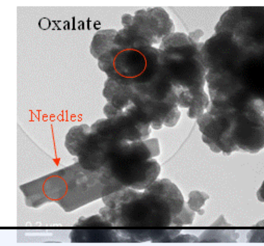
K~30, E_{bd} = 1.5 MV/cm

Energy Density = 2.9 J/cm^3

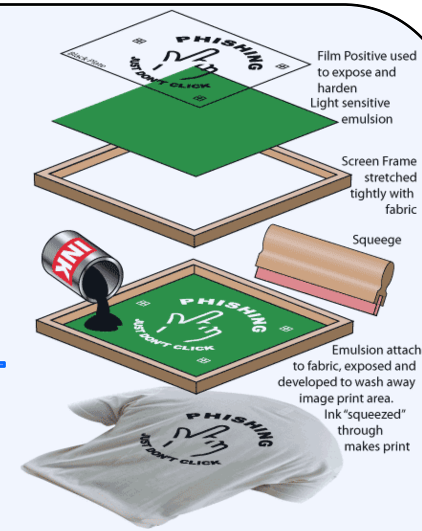
*ICC3, Osaka, Japan, Nov 2010

Current work on CZT90/10

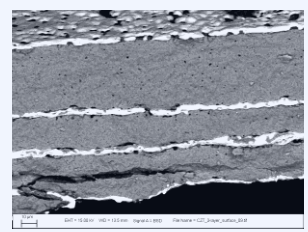
Synthesized powder

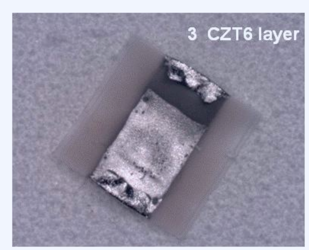


Solution chemistry



Screening printing





multilayer structure

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$Ca(Zr_{0.9}Ti_{0.1})O_3$ Chem-Prep Powder Synthesis Process

$Ca(NO_3)_2 \cdot 4H_2O$/n-ProH

$Zr(OBu^n)_4$ + 2 acac/n-ProH

$Ti(OBu^n)_4$ for $CaTiO_3$ & CZT

CZ Metal Cation Solution

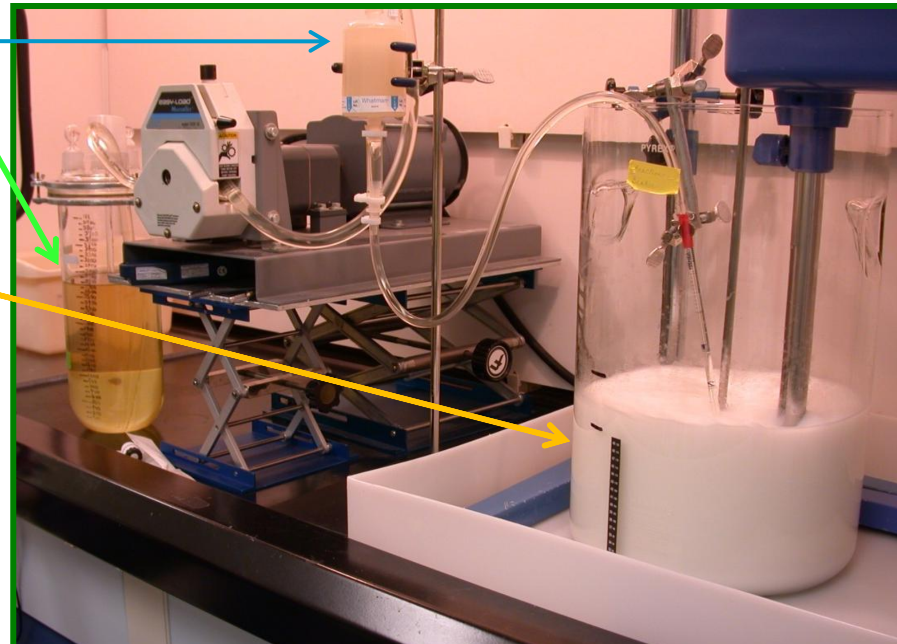
OA/n-ProH precipitant solution

Slurry age 1 hour

Filter Slurry

Oven Dry Filter Cake

Calcine



N-ProH – n propanol
OA – Oxalic Acid

B. A. Hernandez-Sanchez, B. A. Tuttle, et al. Oxalate Co-precipitation Synthesis of Calcium Zirconate and Calcium Titanate Powders, SAND 2009–4743

Advantage: simple, scalability

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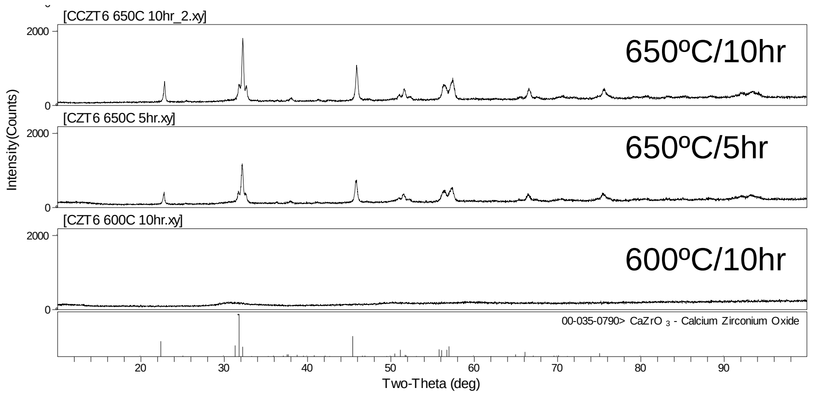
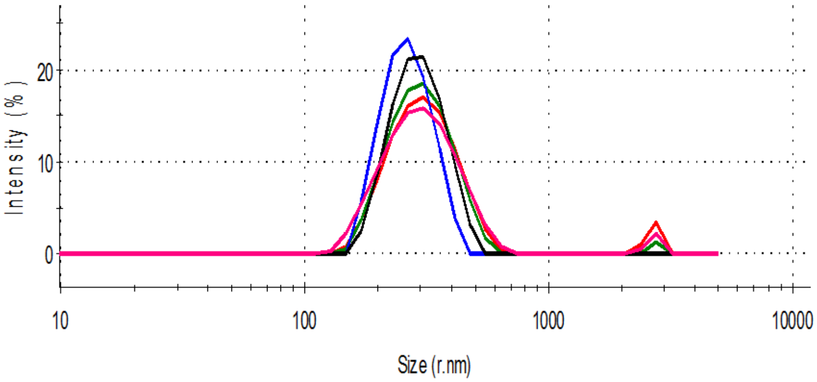
Processing of CZT 90/10

- Calcination: 650ºC/10hr
  - 2.5 hr attrition mill in IPA using PVP-K16 surfactant
  - d_{50} ~ 300 nm
- Pellet
  - 12.5 mm diameter x 1 mm thick
  - 5k Psi uniaxial followed by 30k psi isostatic pressing
- CZT90/10 paste
  - Paste: ESL441 organic vehicle and ESL401 thinner
- Free standing single and multi layer CZT capacitors with Pt achieved by special printing, substrate, setter and cofiring techniques





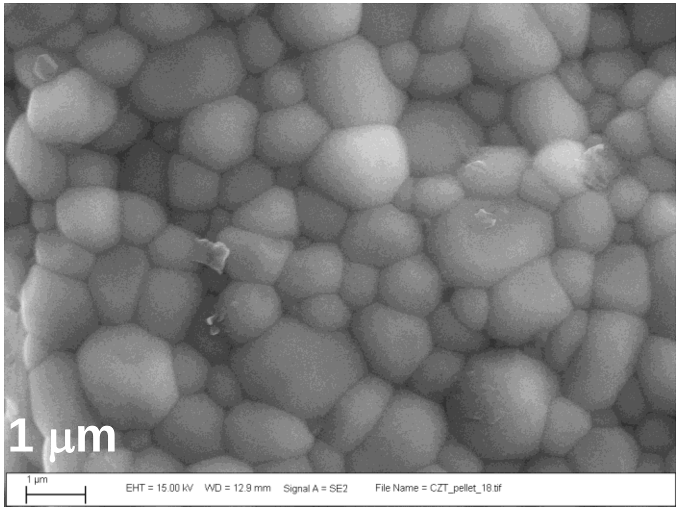
Sintering of CZT90/10

- 2-step sintering for high density and fine grain size*
  - Standard sintering: 1450ºC/1hr + 1350ºC/10hr
- Pellet
  - Reached density 4.04 g/cc
  - Average Grain size ~ 1.0 μm
- Single and multilayer CZT from paste
  - Average grain size ~ 1.5 mm

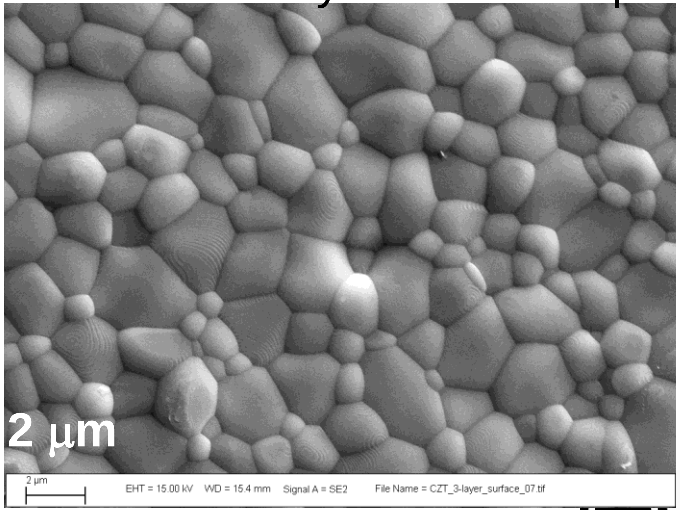
Step 1		Step 2		Pellet density (g/cc)
T (ºC)	t (min)	T (ºC)	t (min)	
1450	5	1300	600	4.00
1450	5	1350	600	3.92
1450	60	1300	600	3.91
1450	60	1350	600	4.04

*I.-Wei Chen & X.-H. Wang, "Sintering dense nanocrystalline ceramics without final-stage grain growth", *Nature* **404**, 168-171 (9 March 2000)

Pellet surface

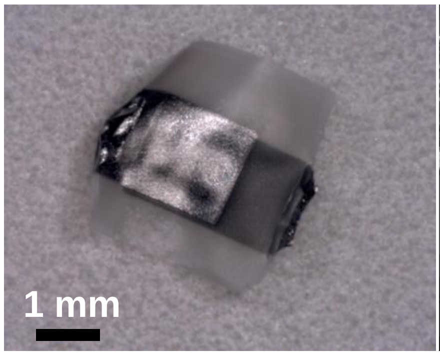


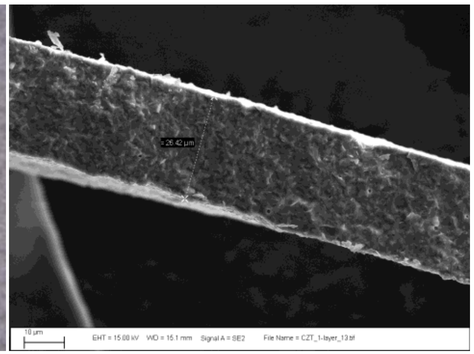
Surface multilayer CZT from paste



Free standing single and multilayer CZT/Pt

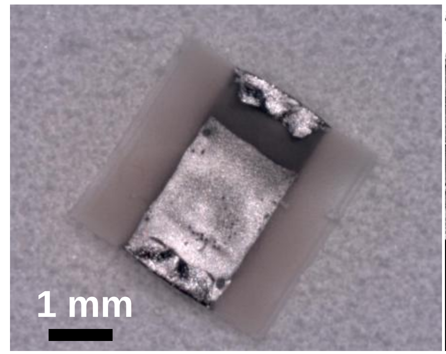
Single CZT6 layer with Pt

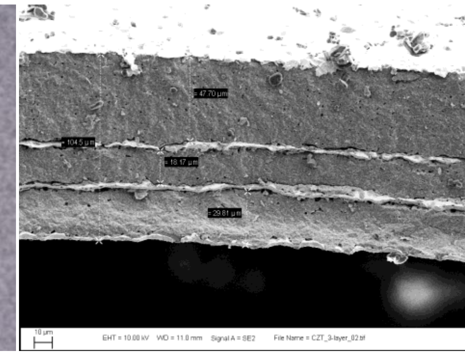




- Used sspecial printing and sintering techniques for free standing Pt cofired CZT90/10
- The CZT layer is nearly transparent → highly dense microstructure
  - Multiple prints per layer
  - Sintered layer thickness ~ 26 μm
- Warping observed, but mostly crack free

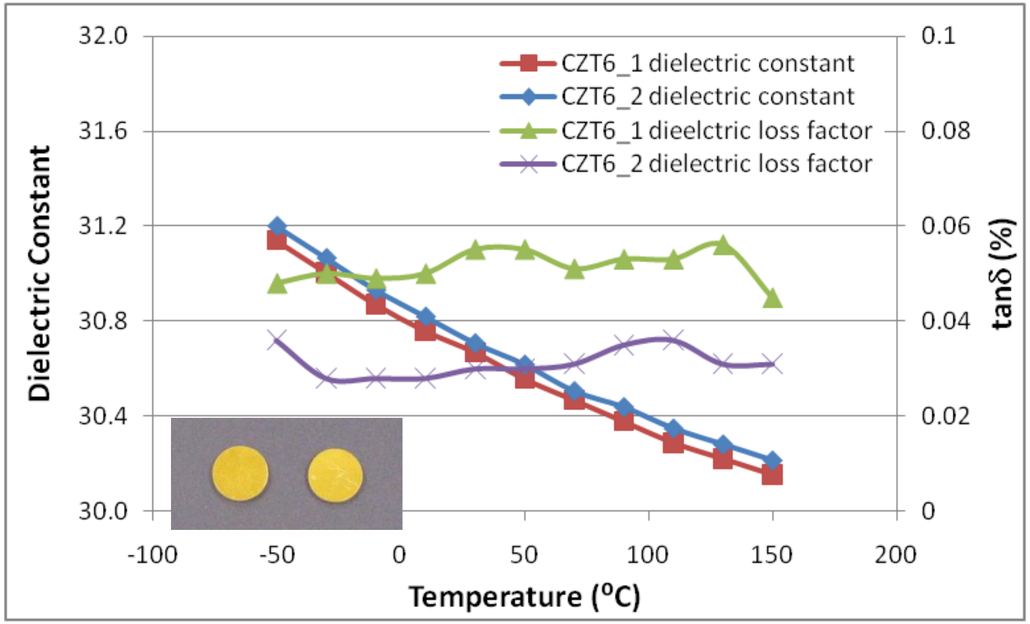
3 CZT6 layers with Pt





- Multilayer build up using a sequential print-dry-print process
- The CZT layer is translucent → highly dense microstructure
  - Sintered layer thickness 18 ~ 48 μm
- Parts mostly flat without significant warping

Dielectric measurement -- pellet



Dielectric properties

- Agilent 4194A, Sigma System temperature chamber
- ε = 31.2 to 30.2 over -50 to 150 ºC @ 1Mhz
  - Very low dielectric loss

Temperature stability

- T_{cc} = -163 ºC/ppm
  - Compare to CZ: ε =27.4 to 27.7 (Tcc = +55 ºC/ppm) over -50 to 150 ºC
- Using linear appx, Tcc ~ 0ºC/ppm @ 2.5 mol% TiO_2
  - Higher than the 1.5mol% TiO_2 by Kell et al., J. Am Ceram Soc. , Vol 57, No 7, P352, 1973

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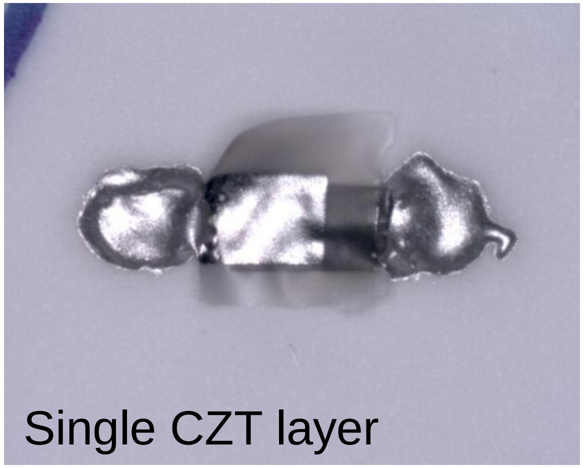
Dielectric measurement – single and multilayer CZT

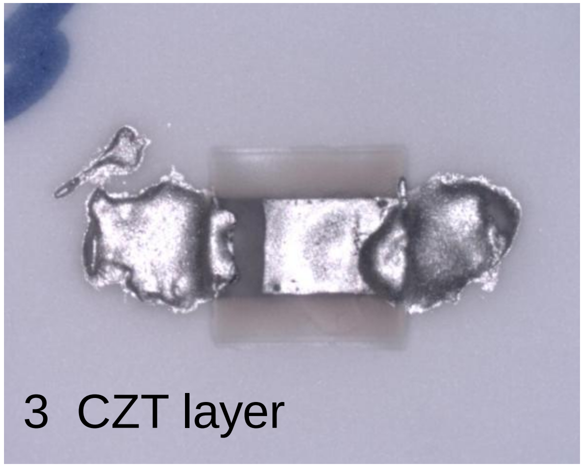
- Samples are mounted on Al_2O_3 substrates with high conductivity Ag epoxy cured at 150ºC/30min
- Agilent 4194A @ 1MHz
- The estimated K of single layer CZT is 34.2, higher than the 31.7 of bulk CZT, possibly due to higher density.
- The capacitance of 3 layer CZT is ~ 3x of that of single layer → scalable

sample	1 layer			3 layers	
	C (pf)	tanδ	Estimated ε assuming d= 26 μm	C (pf)	tanδ
1	46.83	0.034	34.4	135.41	0.037
2	48.85	0.044	35.9	125.10	0.025
3	45.53	0.037	33.4	133.91	0.027

* High ε consistent with SEM observation that there is less porosity in CZT film than the pellet samples



Single CZT layer



3 CZT layer

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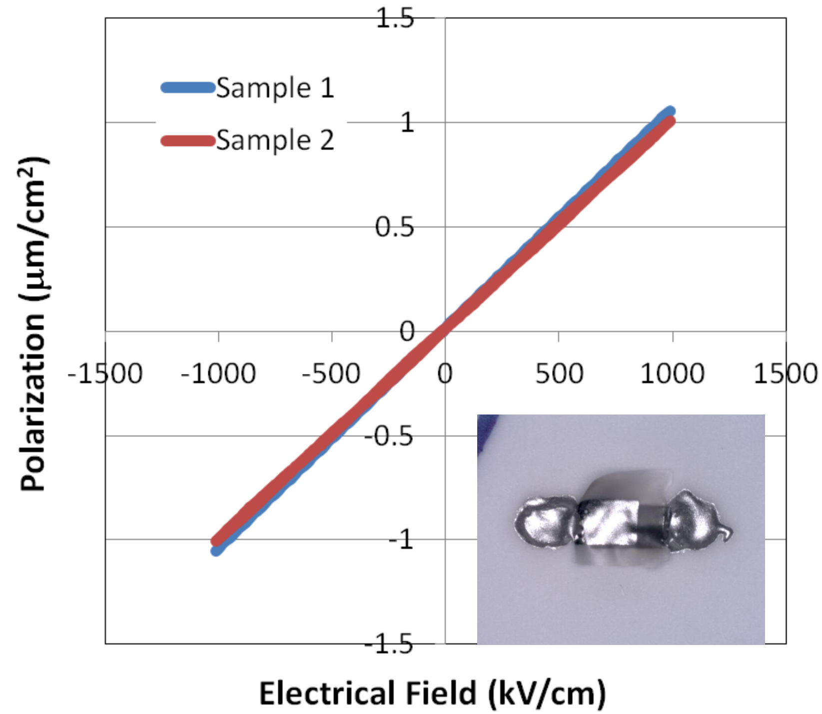
Dielectric breakdown -- single layer

- Standard P-E (polarization vs electrical field) measurement (V_{max} = 10kV) was used to characterize the voltage limit and correspondent energy density

- The single layer CZT samples can constantly withstand 2kV

- Some discharging observed when voltage reaches 3kV

- $E = 1/2 * \varepsilon E^2$



sample	C (pf)	E density @ 1kV (J/cc)	E density @ 2kV (J/cc)	E density @ 3kV (J/cc)
1	47.35	0.30	1.18	2.66
2	47.35	0.30	1.18	2.66

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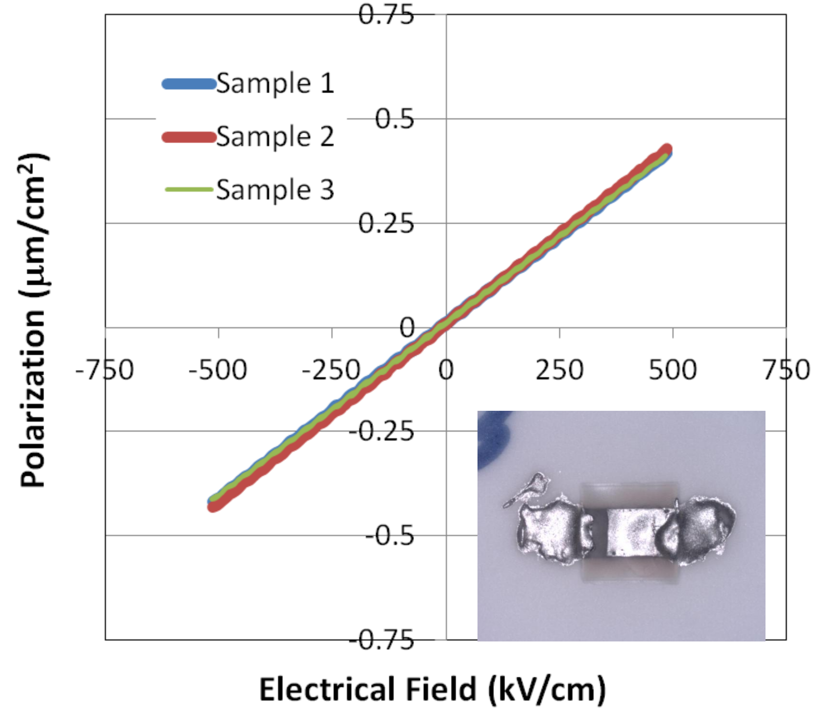
Dielectric break down -- multilayer

- The 3-layer CZT samples can constantly withstand 1kV
- Some discharging observed when voltage reached 2kV
- The lower voltage limit may be attributed to one of the thinner layers in the stack
- Energy density is slighter lower for the multilayer CZT sample



sample	C (pf)	E density @ 1kV (J/cc)	E density @ 2kV (J/cc)
1	120.0	0.25	1.00
2	125.2	0.26	1.04
3	119.2	0.25	0.99

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Summary

- Fine CZT90/10 powder has been synthesized via chemical route
- Free standing, high density single and multilayer CZT/Pt have been fabricated via sequential printing process and special sintering techniques
- The CZT90/10 achieved energy density ~1.2 J/cm^3

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Future Work

- CZT composition with near zero T_{cc}
- Fine CZ and CZT powders by mixed-oxide method
- Low temperature sintering (<1200 ^{o}C) of CZ and CZT ceramics
- Microstructure with high density and small grain size for enhanced dielectric breakdown strength

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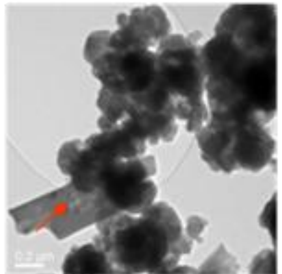
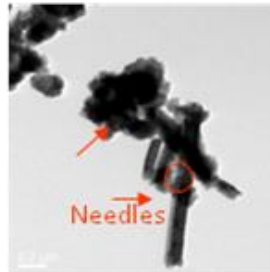
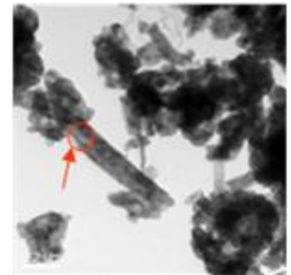
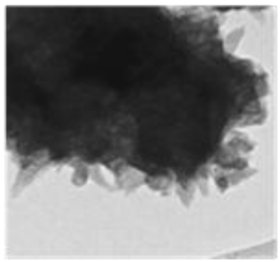
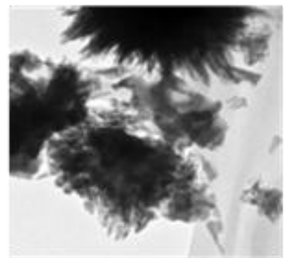
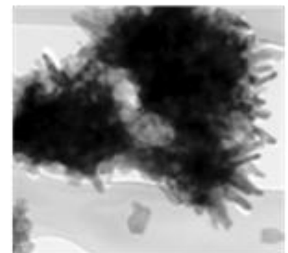
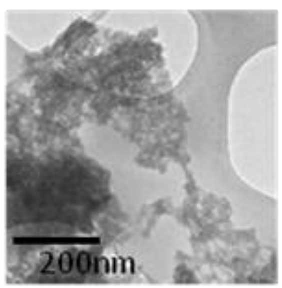
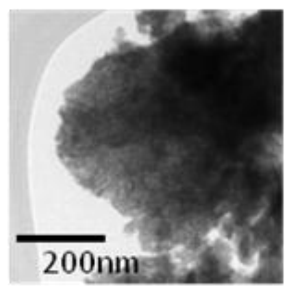
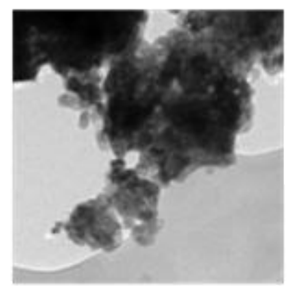
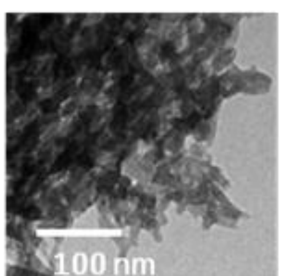
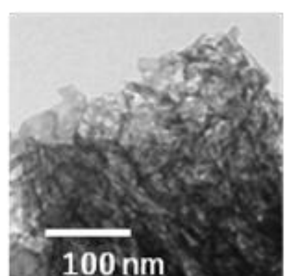
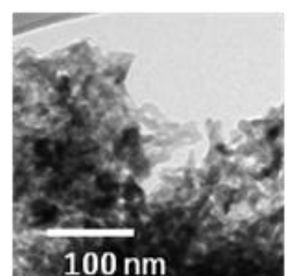
Thank you!

TEM Images of Resulting Powder Morphology and Size After Heat Treatments

Sample	Oven Dried Oxalate	Pyrolyzed	Calcined	
$CaZrO_3$	 200nm	 200nm	 200nm	EDS and diffraction studies indicate needles are $Ca_{0.15}Zr_{0.85}O_{1.85}$ while spherical powder is $CaZrO_3$.
CZT 90/10				Presence of $Ca_{0.15}Zr_{0.85}O_{1.85}$ again shows up in needle or wire shape for CZT 90/10.
CZT 30/70				Lowered Zr stoichiometry of CZT **30/70** did not have needles.
$CaTiO_3$				$CaTiO_3$ powders had only agglomerated powders.

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