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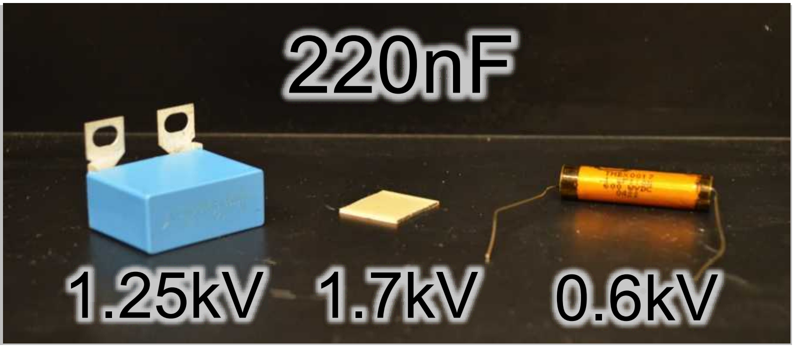

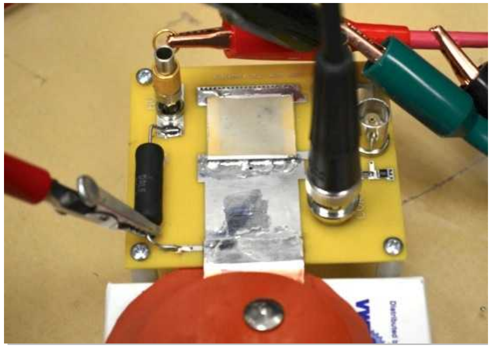

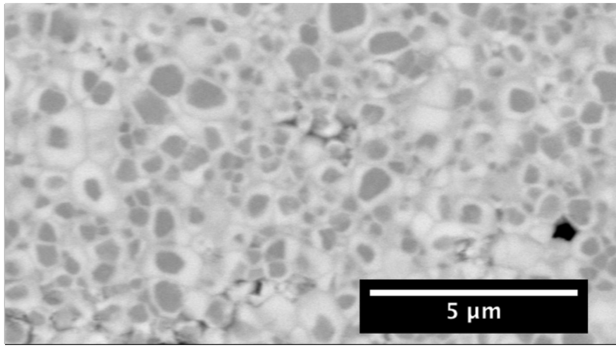

Pulsed discharge behavior of $(Bi_{0.2}, Ba_{0.8})(Zn_{0.1}, Ti_{0.9)})O_3$ -based relaxor multilayer ceramic capacitors

H.J. Brown-Shaklee, John J. Borchardt, Mia A. Blea and G.L. Brennecka

Material Science and Engineering Center Sandia National Laboratories, Albuquerque, NM USA

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We are studying weakly coupled relaxors for high energy density capacitors

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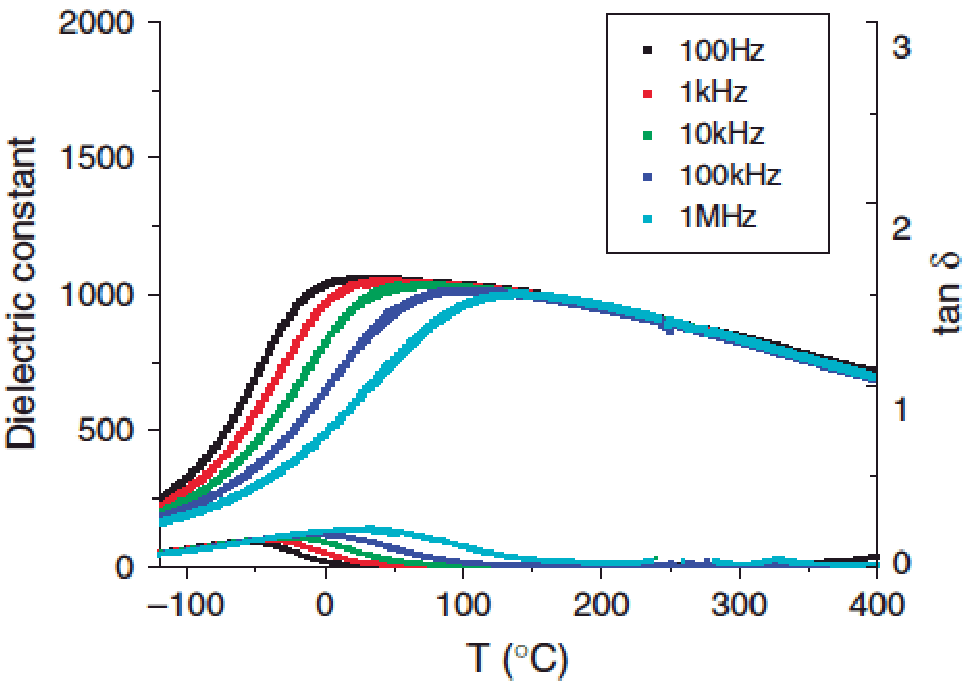
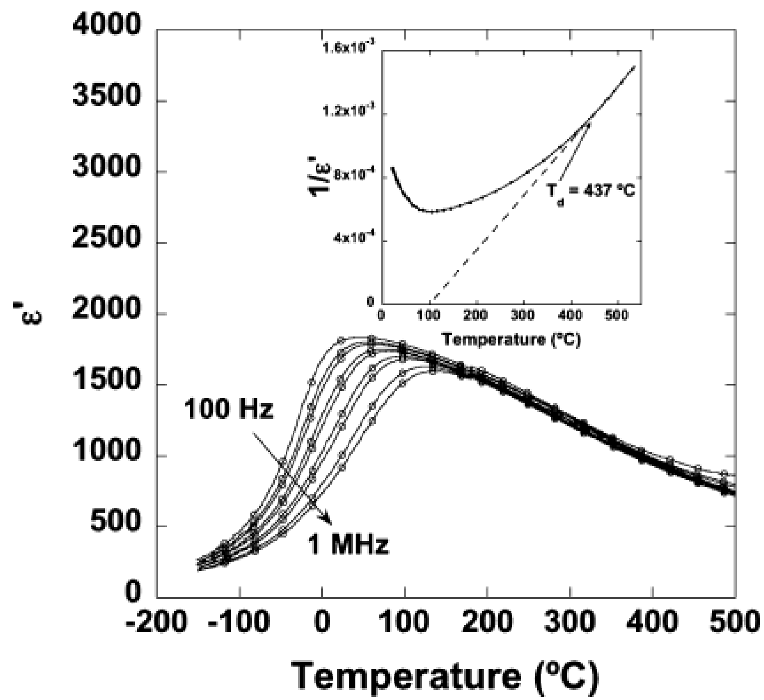
$BiScO_3$-80$BaTiO_3$



$BiZn_{½}Ti_{½}O_3$-80$BaTiO_3$



These so called weakly coupled relaxors exhibit high permittivity and can exhibit low dε'/dT above the relaxation temperature

PSU Ogihara, Randall, and Trolier-McKinstry, JACerS **92** [1] 3554-61 (2009)

OSU Raengthon and Cann, JACerS **95** [11] 3554-61 (2012).

Why do we need high permittivity dielectrics?

High Energy Density Dielectrics

DC and Pulsed DC → **Power Quality and Smoothing**

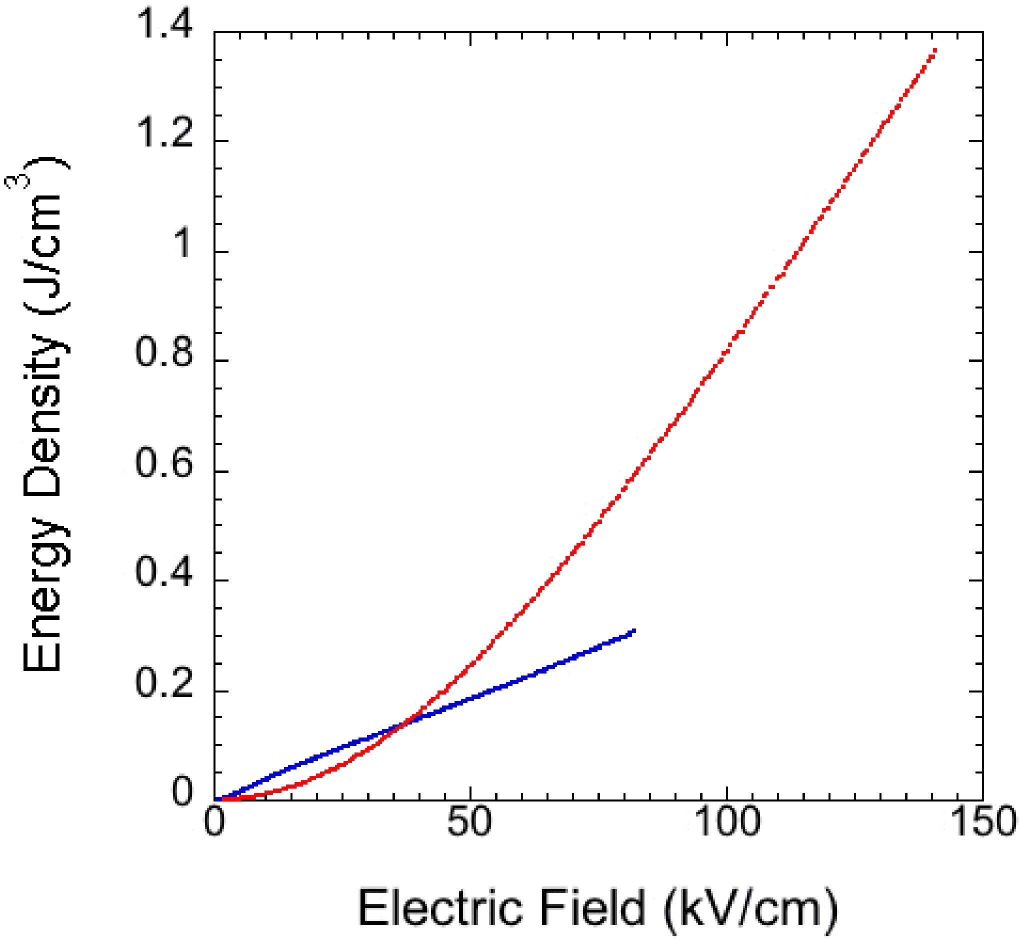
AC → **PV Inverters (Wide Frequency AC)**

Why high energy density dielectrics?

Power Quality and Smoothing		PV Inverters
Low electro-mechanical response	Chemical	Inexpensive
Temperature stable	⟷	Temperature stable >200°C
Reliable	"Doping"	Reliable

Can’t we just use $BaTiO_3$?

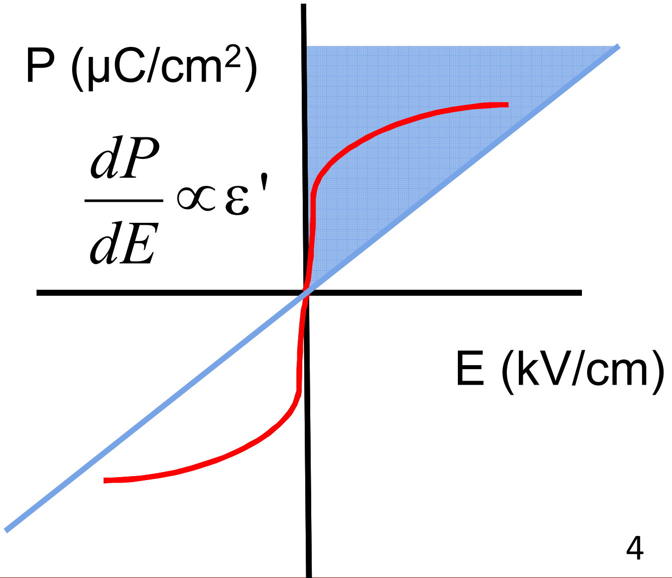
- Commercial capacitors exhibit electric field tuning
  - Dielectric constant changes with applied field
  - Commercial capacitors are optimized for high ε‘ but not energy density



Energy stored in a capacitor is:

$$W = \frac{1}{2}\varepsilon_r\varepsilon_0 \frac{A}{d} V^2$$

$$\left(\frac{J}{cm^3}\right) = \int_{E_0}^{E_{max}} P(E)\,dE$$



$$\frac{dP}{dE} \propto \varepsilon'$$

Reliable high capacitance multilayer capacitors are required for grid surety

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Goals

1. Develop MLCCs based on the $Bi(Zn_{0.5}Ti_{0.5})O_3$ –$BaTiO_3$ system that exhibit favorable voltage tuning behavior
2. Study the dielectric relaxation in frequency *and* time domains
    a) Moderate piezo response
    b) Forward Fourier transform reveals dominant frequency components from a time domain signal
    c) Superposition does not hold for circuits containing non-linear capacitive elements
3. Adjust chemistry to achieve widest possible operating temperature window for AC *and* pulsed DC applications

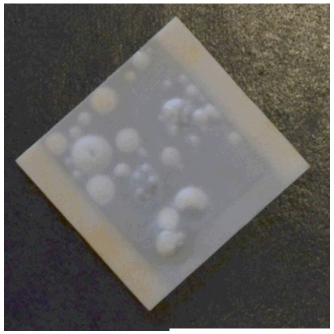
200nF MLCCs were fabricated in house

200nF MLCC

- BZT-BT powder was synthesized from $BaCO_3$, Bi_2O_3, ZnO, and TiO_2
- Powders were calcined at 950°C for 12 hrs in air
- Particle size was reduced by ball milling
- Milled powders were blended with Ferro B-73305 PVB-based binder
- 15.25 cm wide tapes were cast on a heated bed
- Tapes were printed with DuPont 9894 Pt-Ink
- Sample burnout in flowing O_2 and sintering in stagnant air

Blistered 200 nF MLCC were fabricated initially

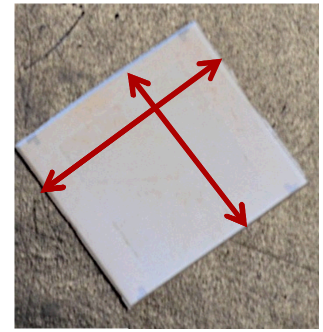
MLCC sintered at 1210°C



Reduced sintering temperature

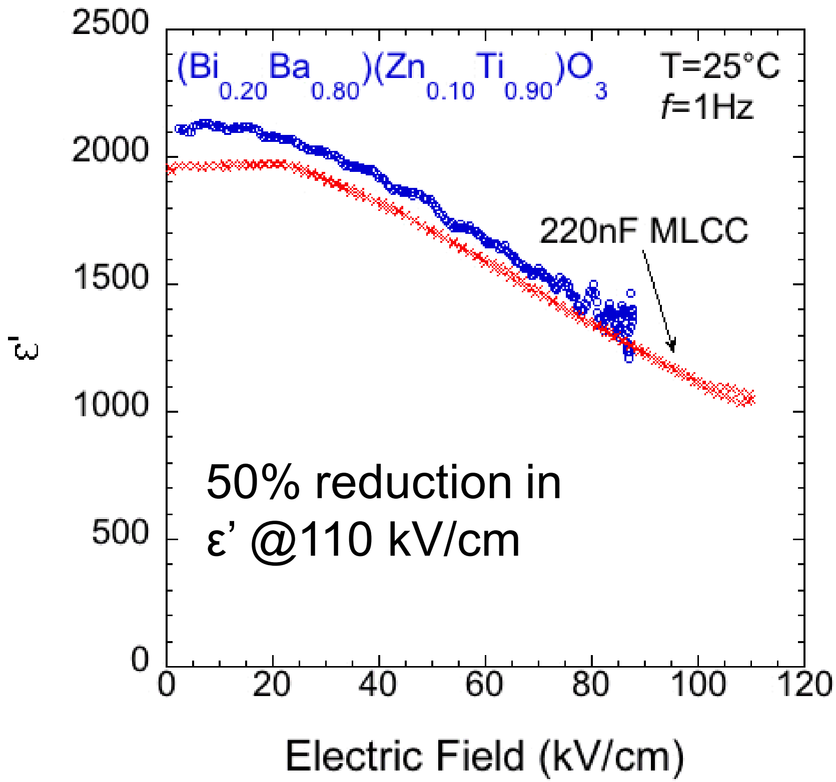
No blisters

MLCC sintered at 1040°C



Systematic study eliminated blisters in MLCCs

RGA indicated that O_2 was released above 1000°C!

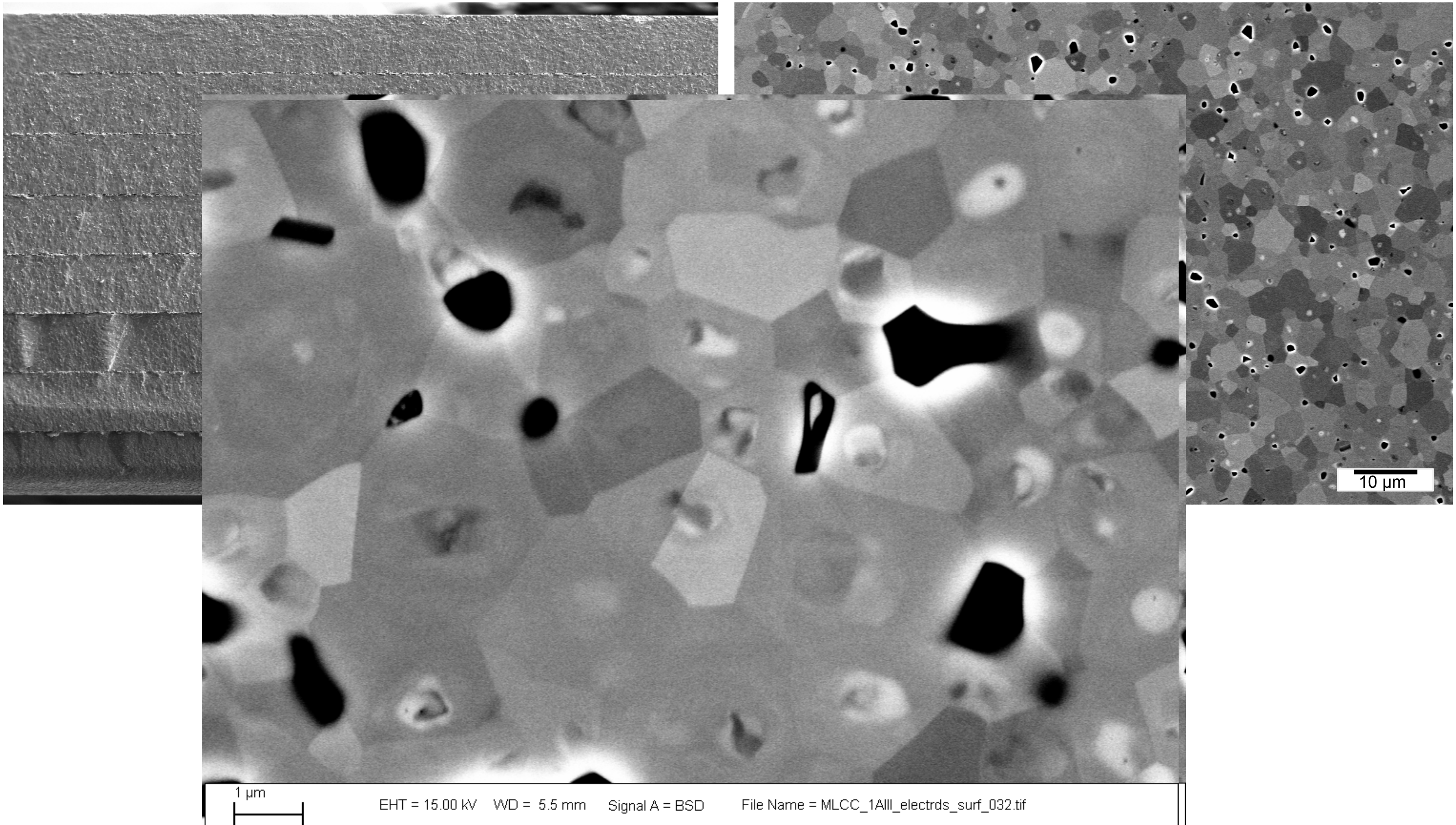


L = 22.68 mm
w= 24.4 mm
t = 1.12 mm

6 active layers
9894 Pt ink with BZT-80BT dielectric

Final dicing can reduce package size (fiducials painted in Pt on top of MLCC)

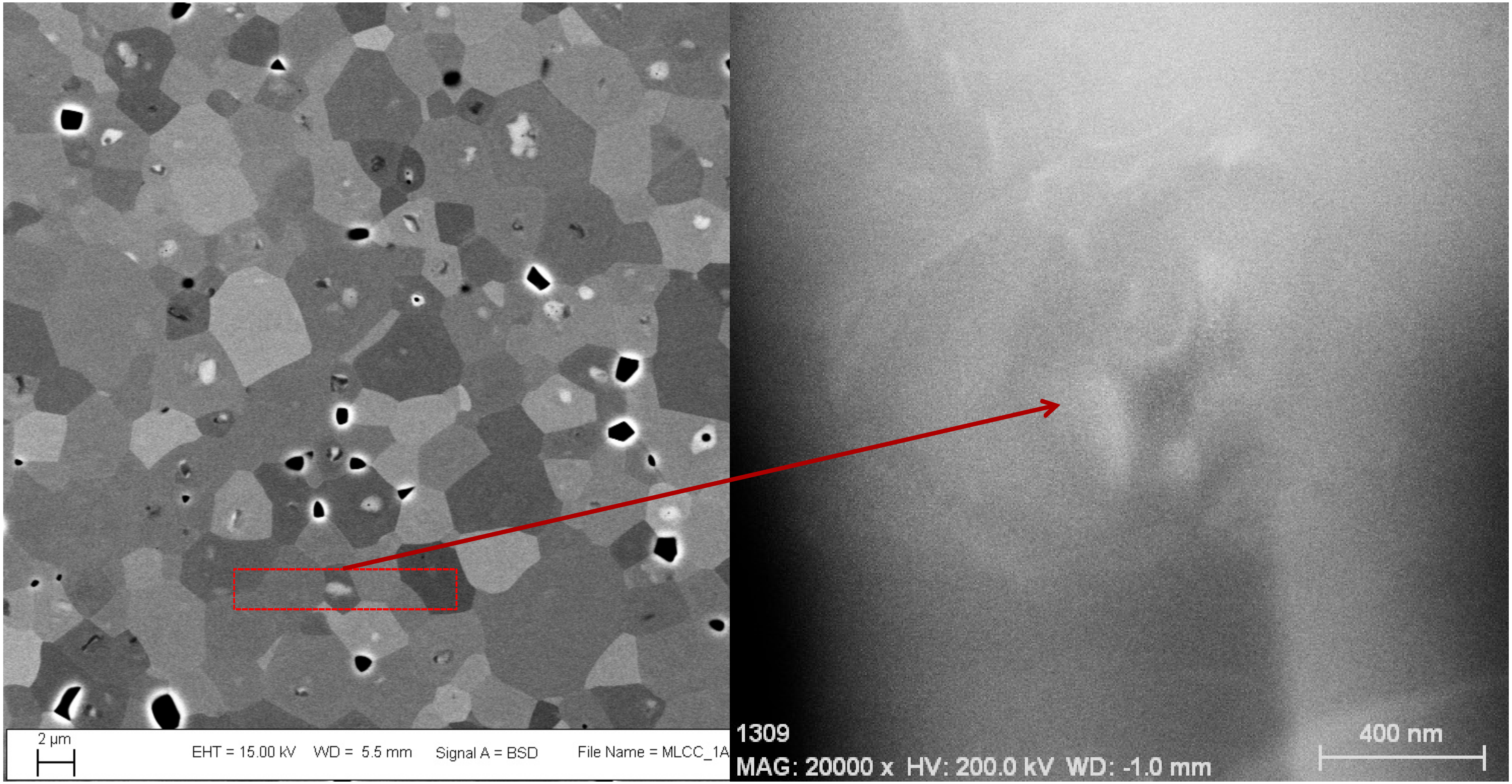
MLCC dielectric exhibits high-Z (bright) core



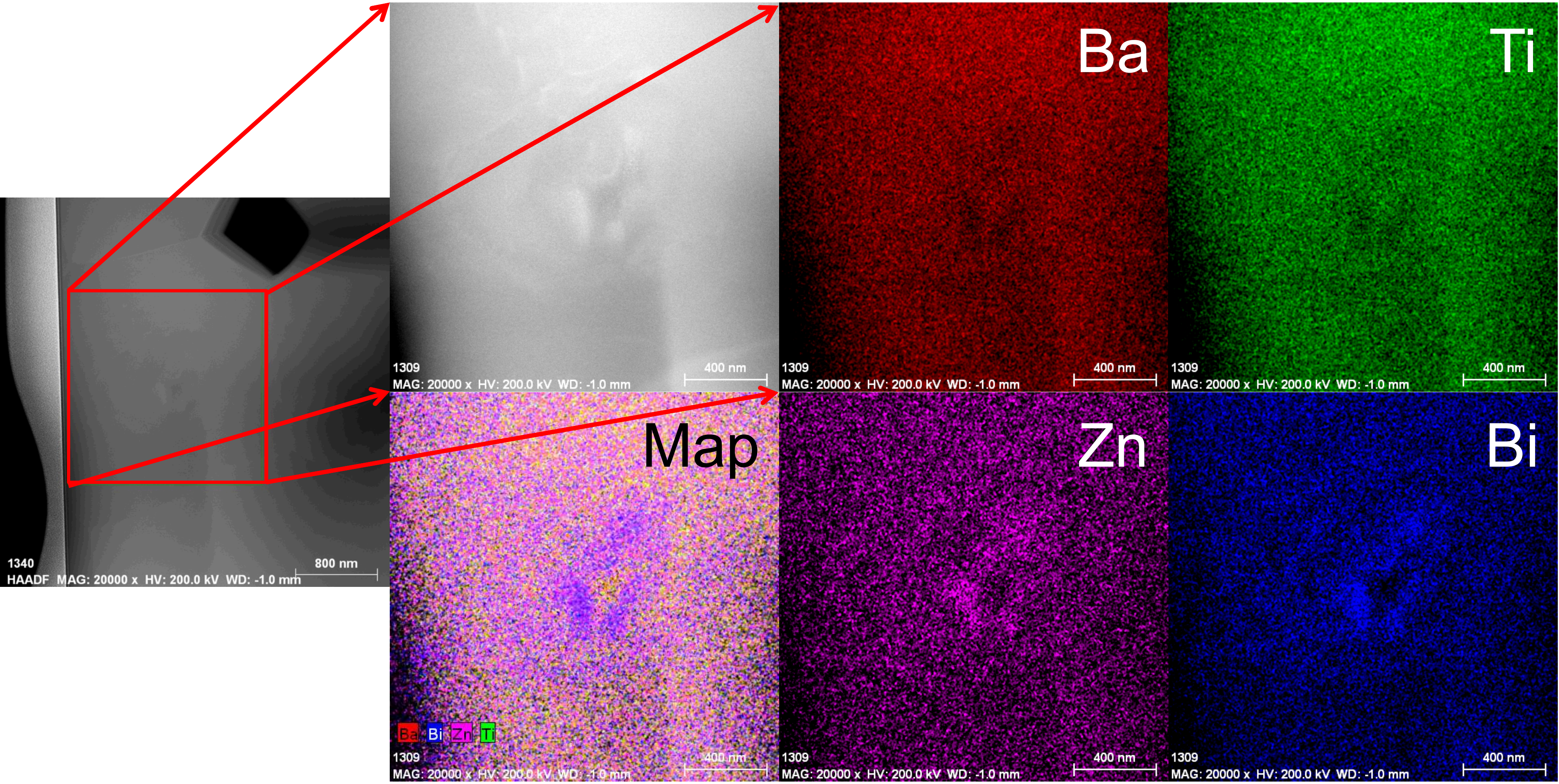
Possible domains (twins) in microstructure

TEM reveals same core-shell compositional gradients

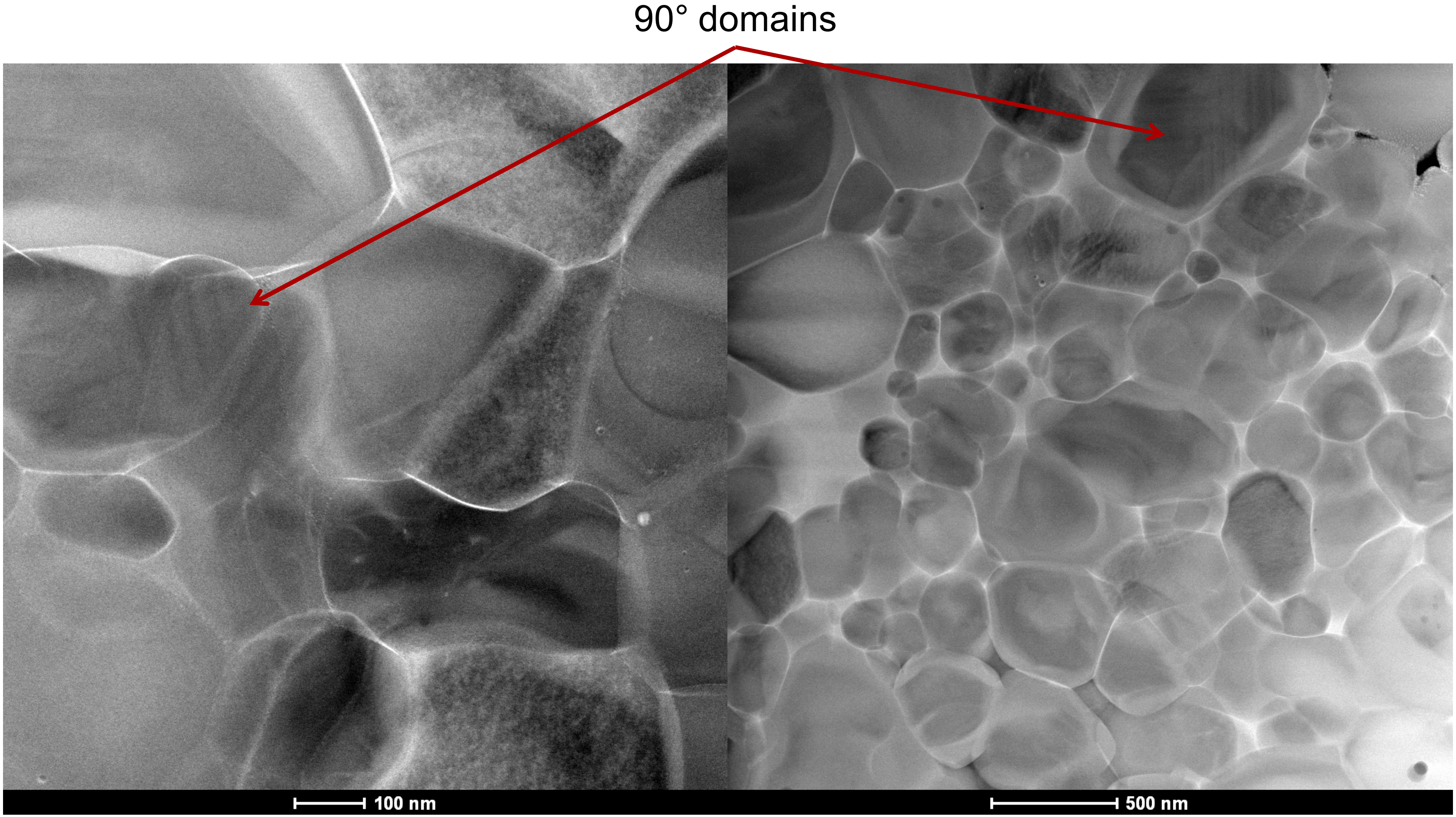
SEM | HAADF TEM



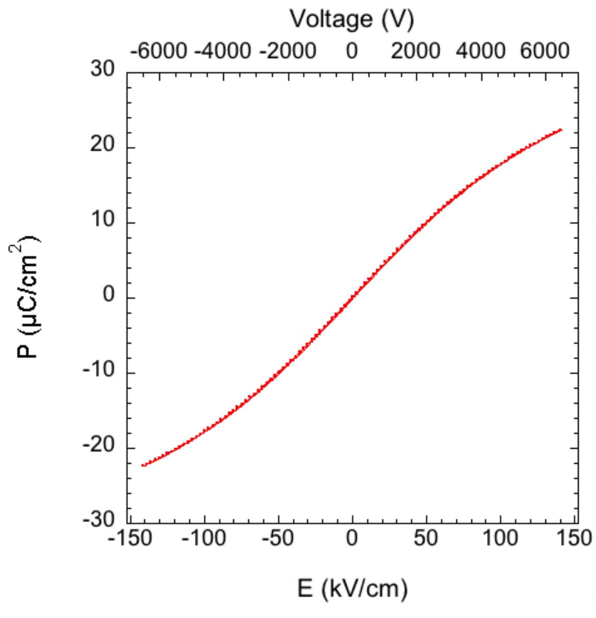
STEM EDS mapping revealed Bi and Zn segregation



HAADF also reveals presence of 90° domains in pseudo-cubic BZT-BT



Energy densities of >1.3 J/cc have been demonstrated



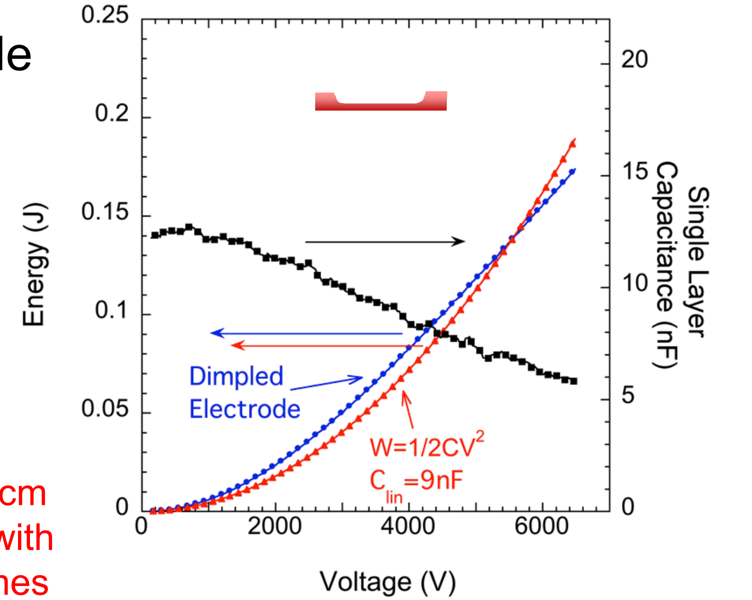
Dimpled Electrode

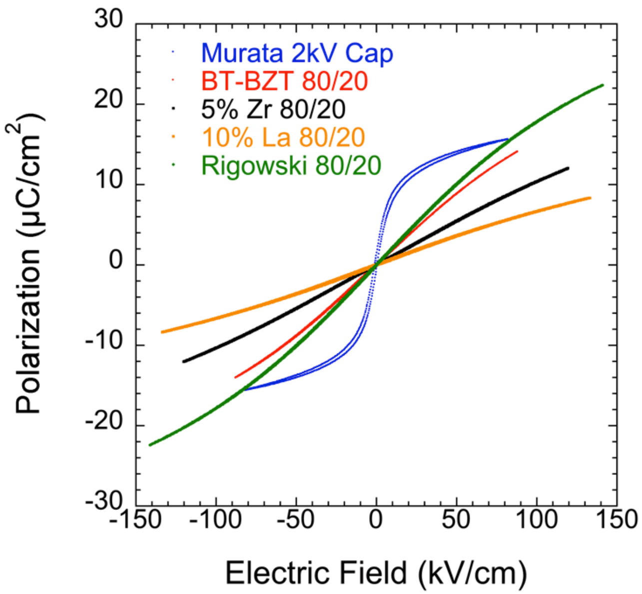
t=460µm
A=2.77cm^2
v=0.127cm^3

$E/v_{100kv/cm}$=0.82 J/cm^3

$E/v_{140kv/cm}$=1.35 J/cm^3

Breakdown >230 kV/cm have been achieved with smaller sample volumes

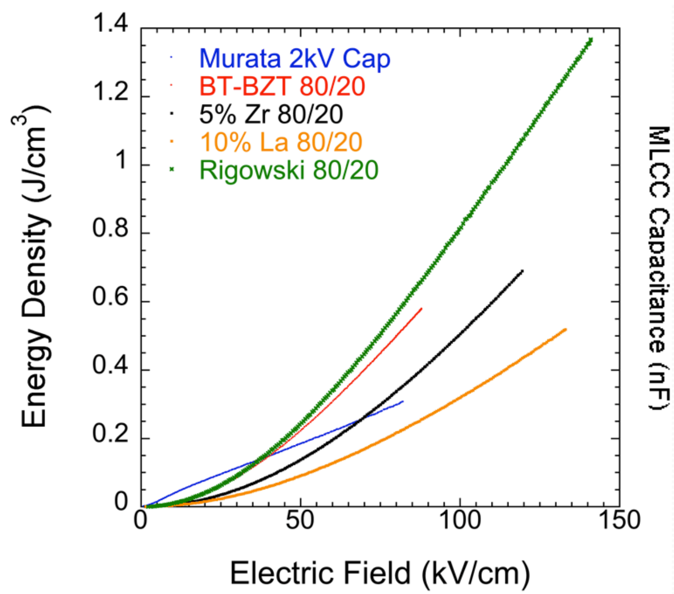




200nF MLCC

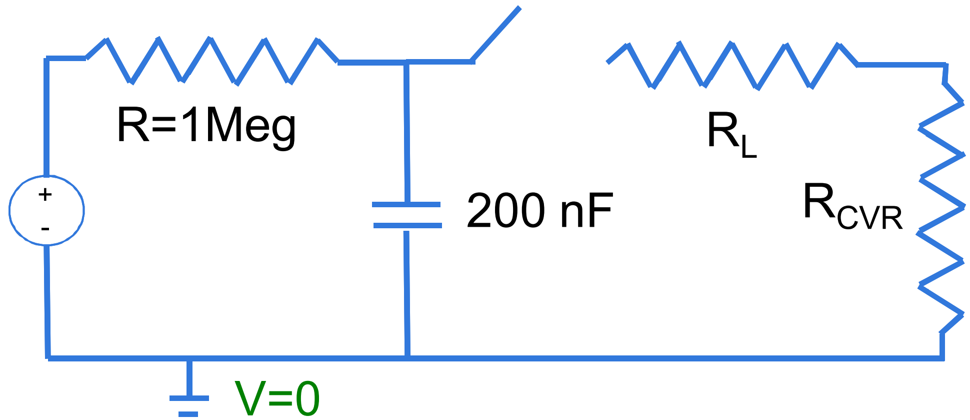
t=135µm
A=18.1cm^2
v=0.262cm^3

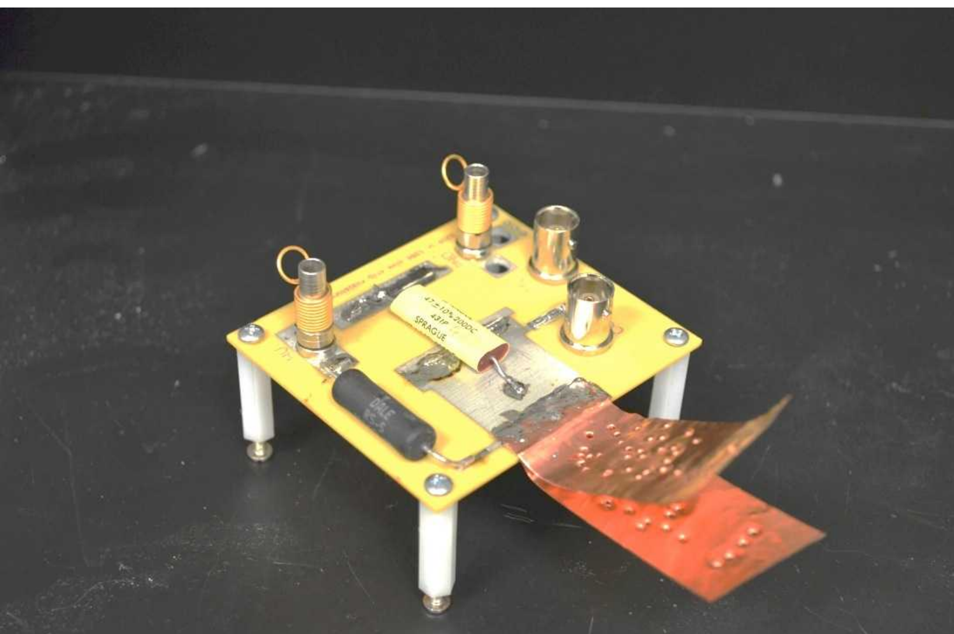
$E/v_{100kv/cm}$= 0.69J/cm

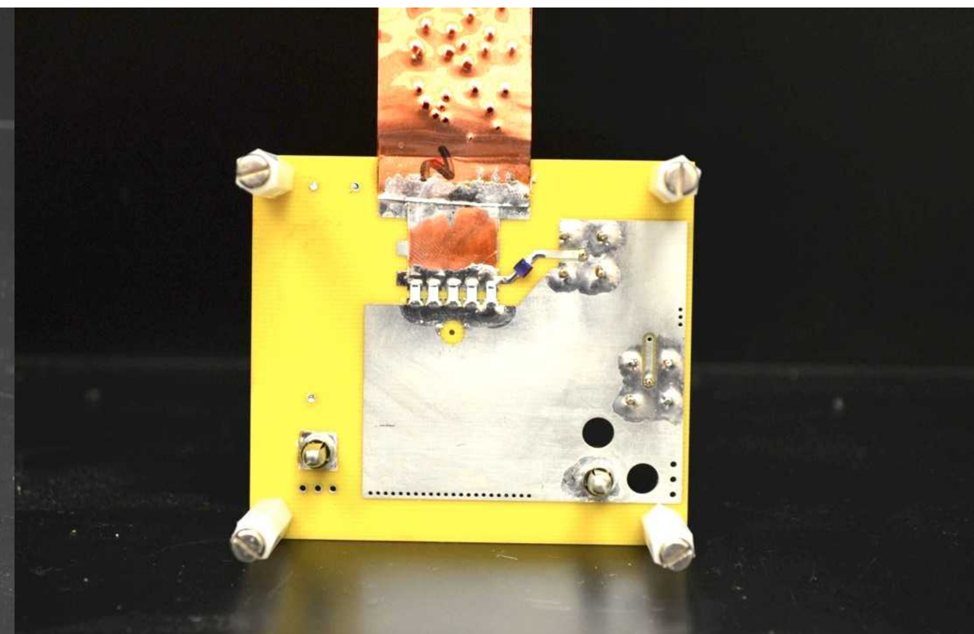


We are interested in pulse discharge behavior as well

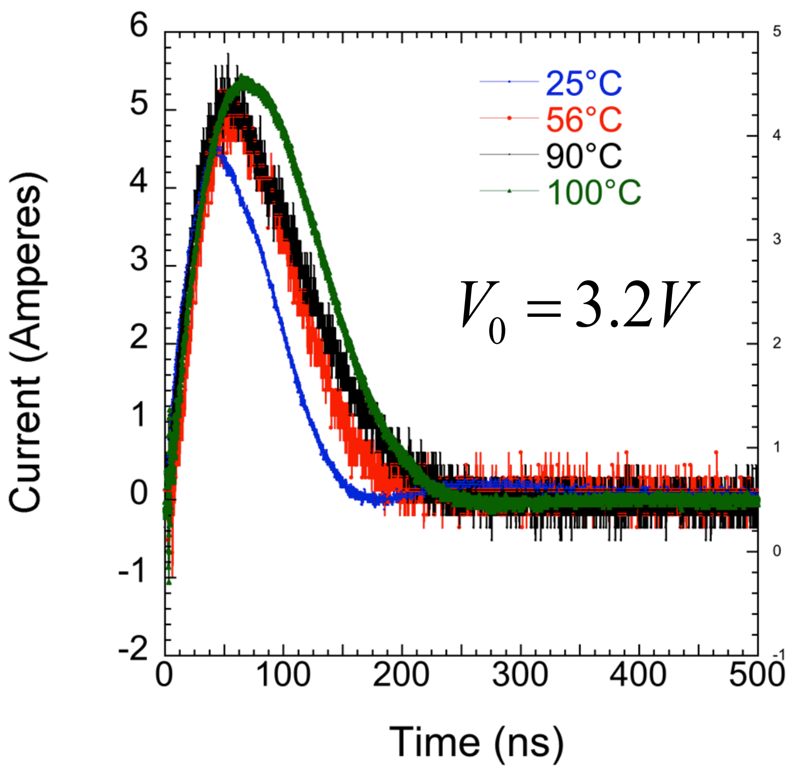
Most measurements we make are in frequency domain but pulse discharge occurs in the time domain…

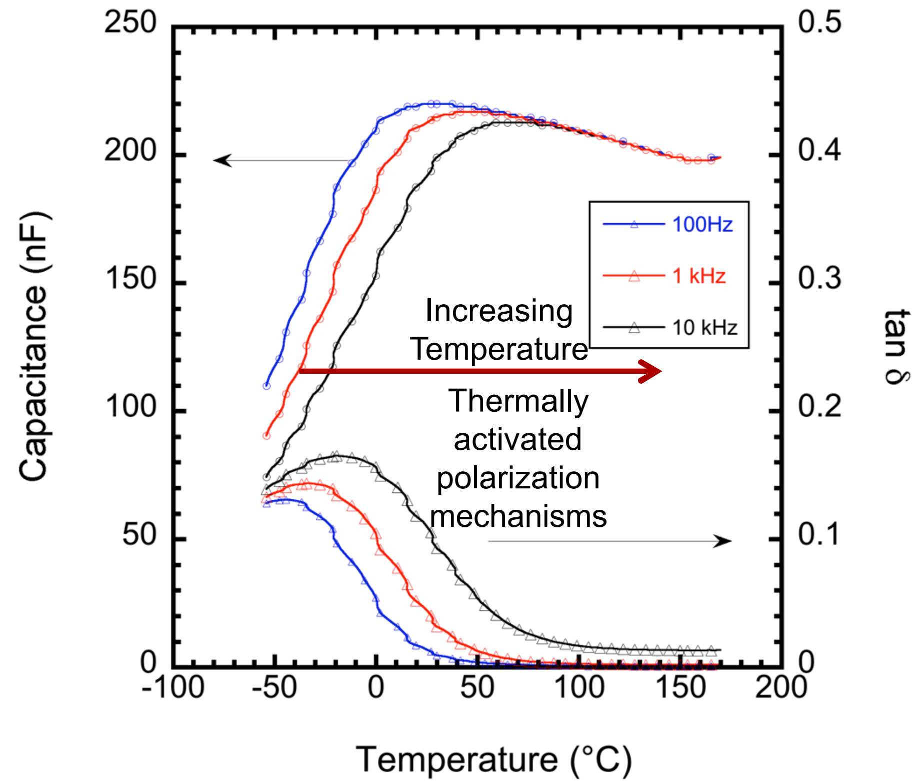






Waveform shapes changed with increasing temperature



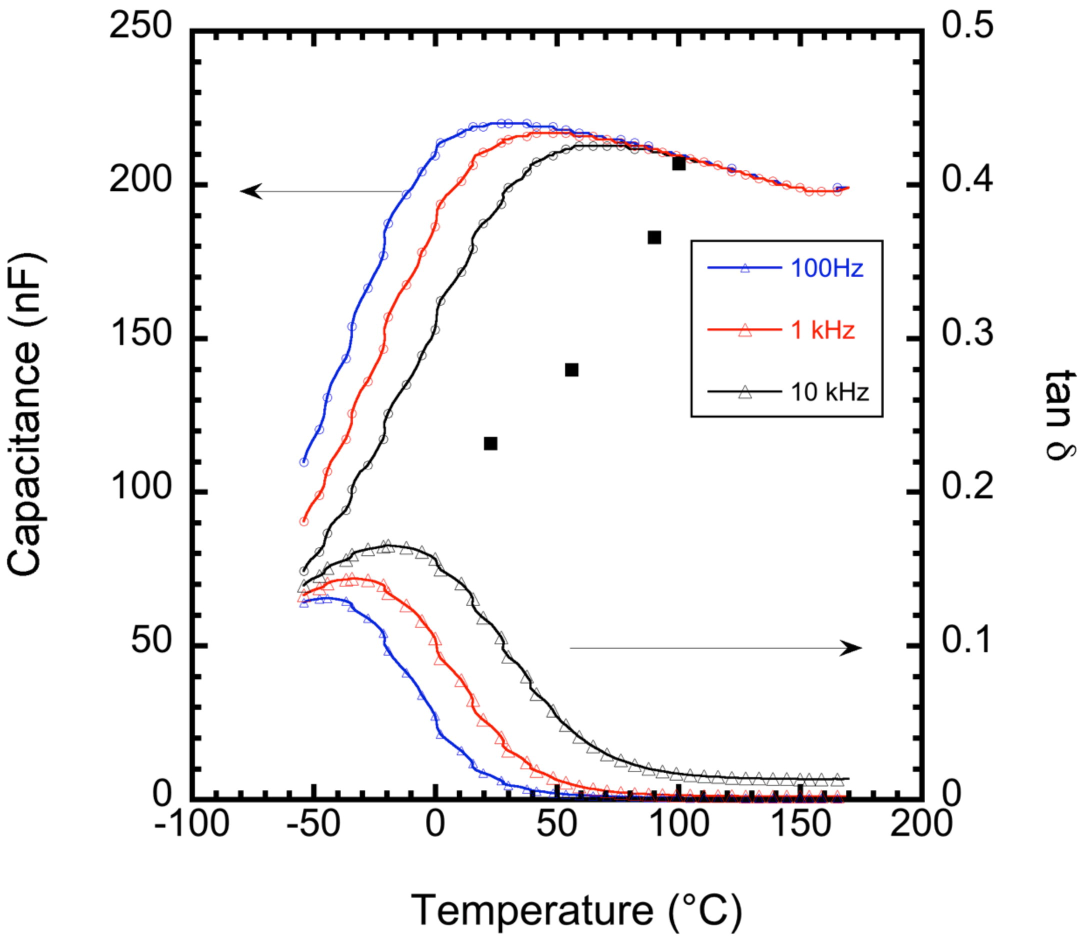


Loss of small signal between 200 and 300 ns with increasing temperature…thermal activation of slow polarization mechanisms

Capacitance appears to increase with temperature (higher peak current)

Dielectric relaxation was also shown at elevated temperatures

Frequency Domain



Time Domain

Temperature (°C)	C_{2MHz} (nF)	C_{10mHz} (nF)
-55		170
-40		159
-30		214
10		
22.5	116	208
56	140	
90	183	
100	207	

$$\omega_0 = \frac{1}{\sqrt{LC}}$$

The energy stored by the MLCC must equal the energy dissipated during discharge

MLCC, 3.2V, 56°C

Stored (DC charge)

$$E = \frac{1}{2} c V^2$$

$$E = \frac{1}{2} 142nF(3.34Volts)^2 = 7.92x10^{-7} Joules$$

Dissipated during discharge by circuit resistance

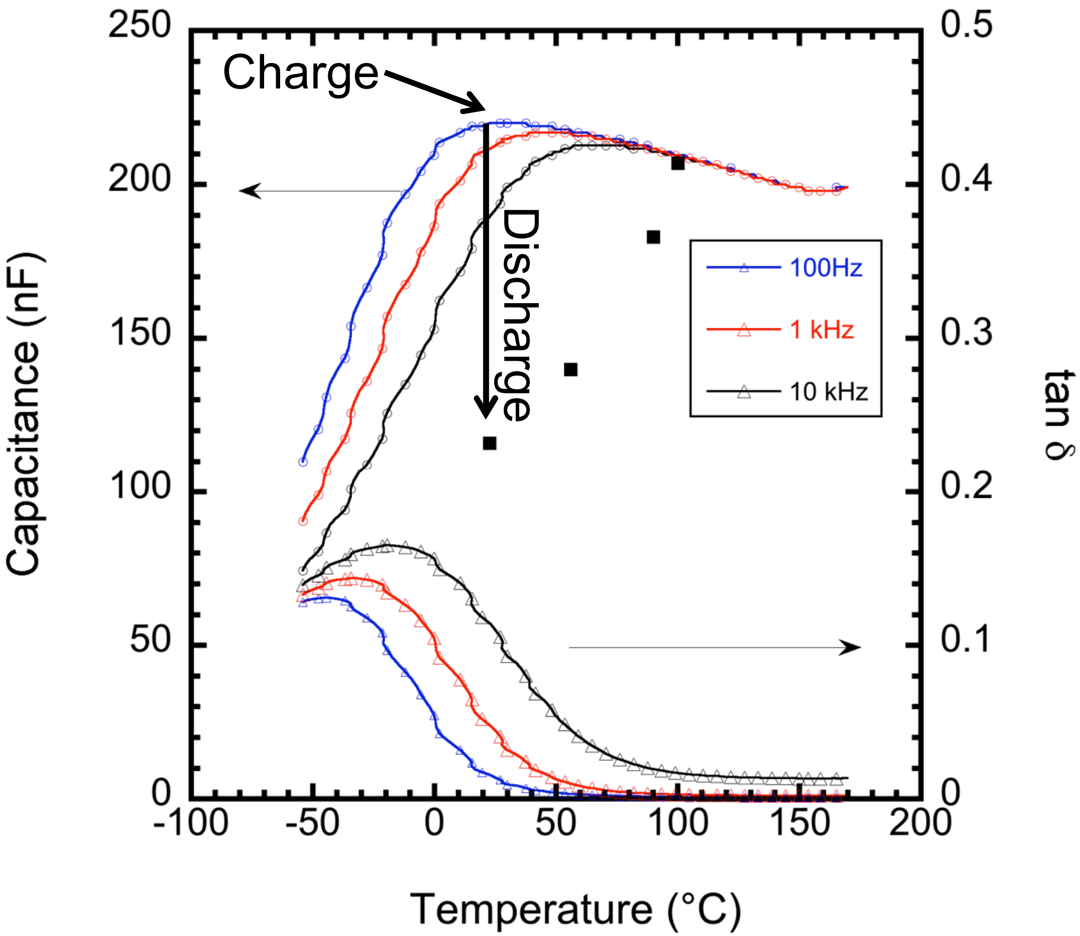
$$E_{discharged} = R \int_{t=0}^{t=dis.} i_{CVR}^2 \, dt$$

$$E = 474\Omega \int i(t)^2 \, dt = 8.22x10^{-7} Joules$$

The values agree to within 96%
220nF polymer cap agrees to within 99%

We still don’t know where 40% of the energy went from the effective low-*f* charge and high-*f* discharge

Combining frequency and time domain data



The charge capacitance should be:

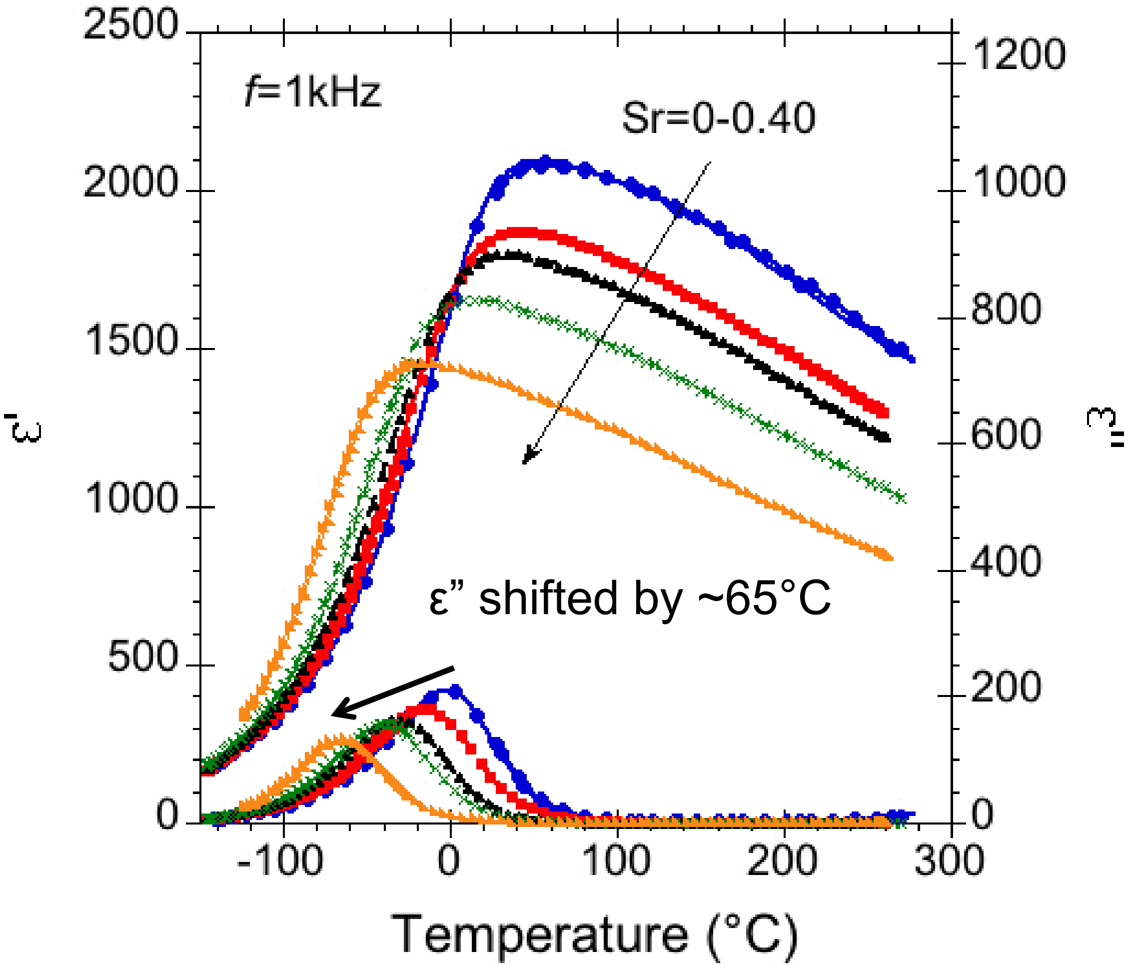
$$E = \frac{1}{2} c_{low-f} V^2$$

The discharge capacitance should be:

$$E = \frac{1}{2} c_{high-f} V^2$$

Dielectric loss only accounts for <15%

Sr shifts T_{max} below room temperature



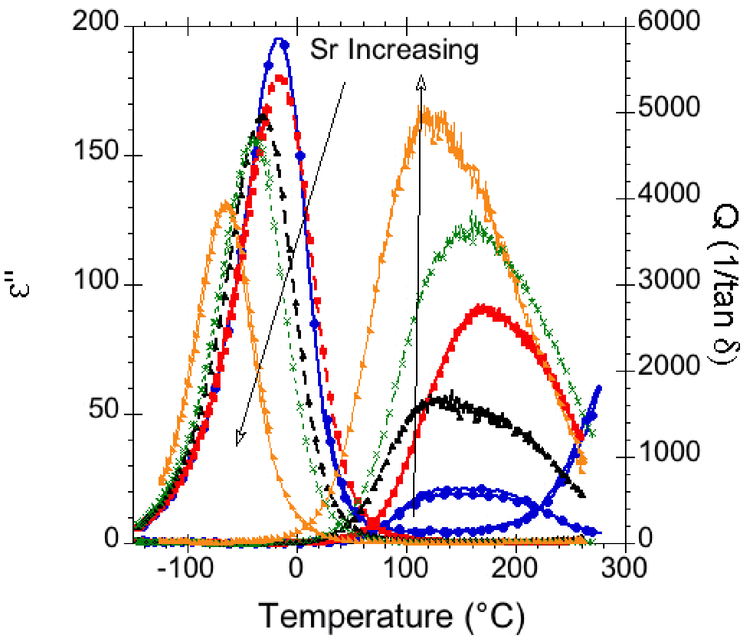
Sr (%)	TCε' (ppm/K)
0	-1338
5	-1464
10	-1479
20	-1474
40	-1603

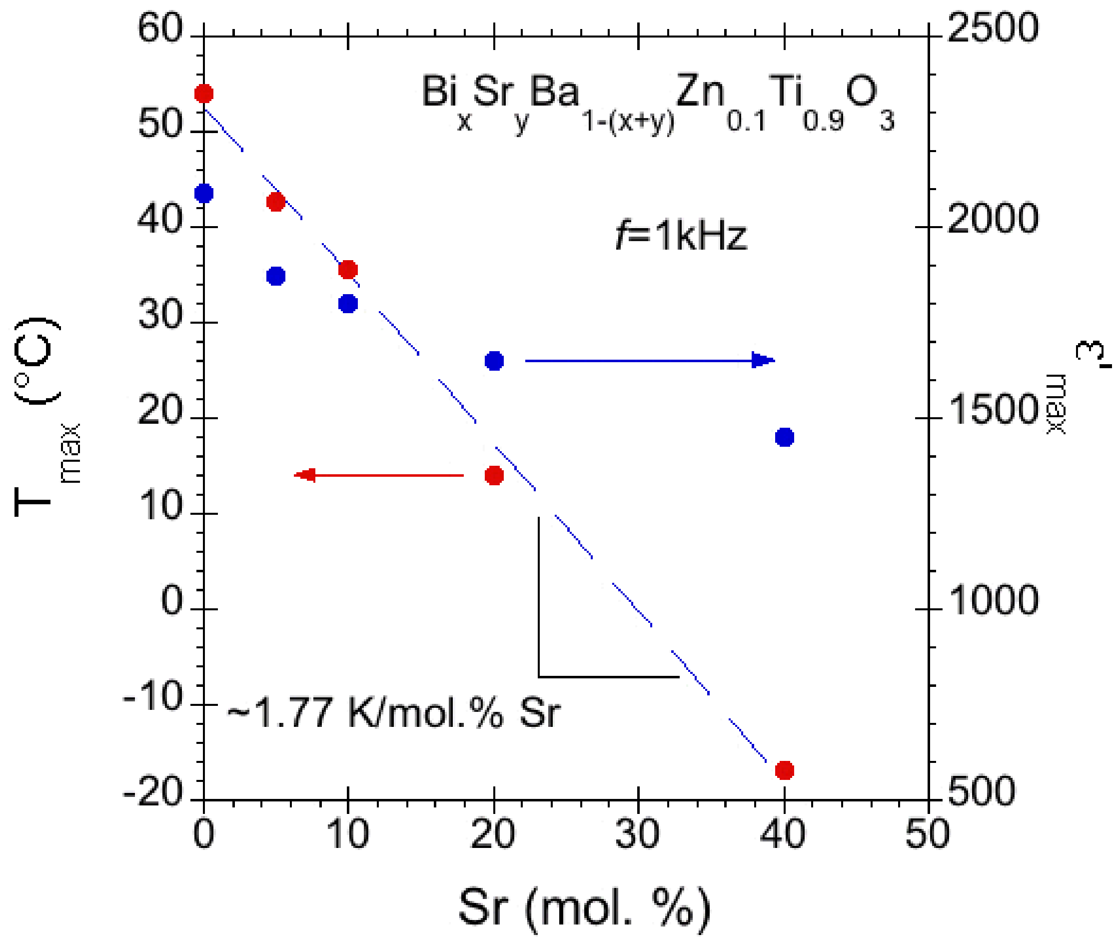
$$TC\varepsilon' = \frac{-(\varepsilon'_{max} - \varepsilon'_{max@+180°C})}{\varepsilon'_{max@+90°C}(180°C)}$$

- Dielectric relaxation should be below 0°C for high frequency and fast pulse applications

Sr shifts T_{max} by 1.77 K/mol.% Sr

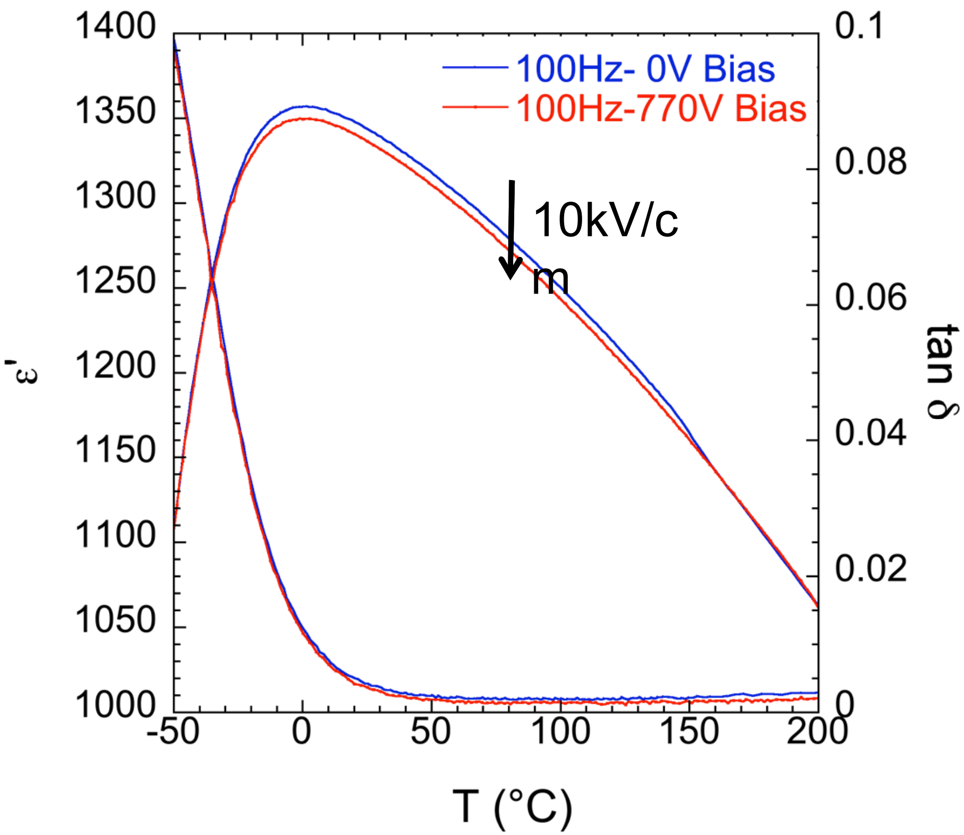
- X7R (-55 to 125°C) window is not achievable with Sr substitution
- Sr decreases loss

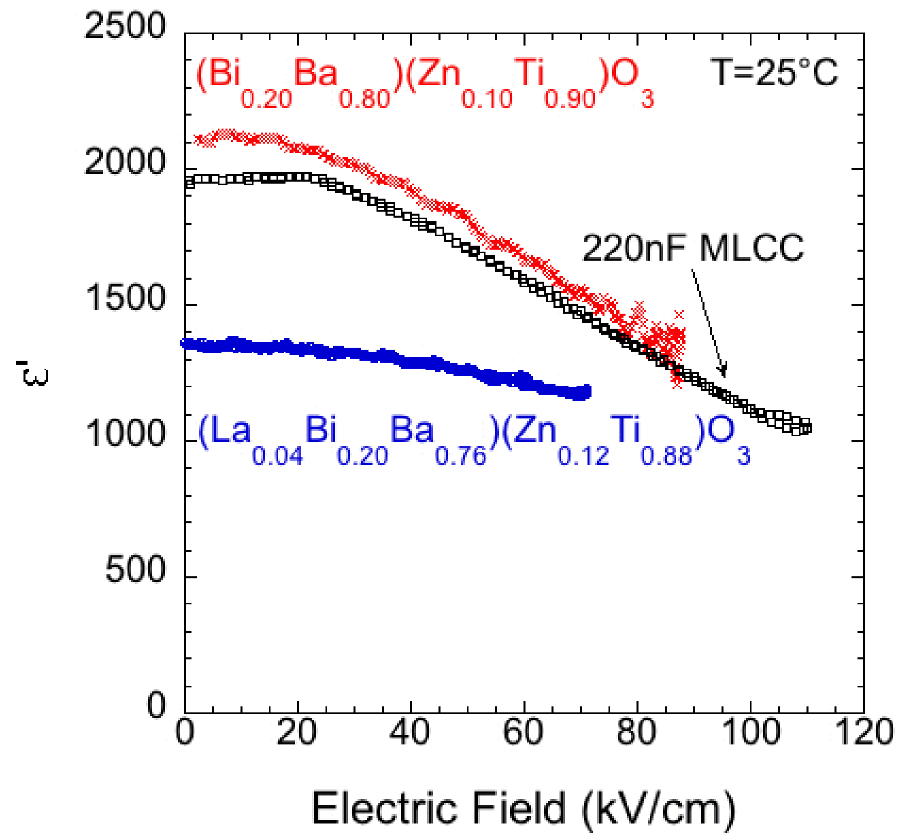




Sr in BST shifts orthorhombic to tetragonal transition by ~2K/mol.%

Composition also affects voltage tuning

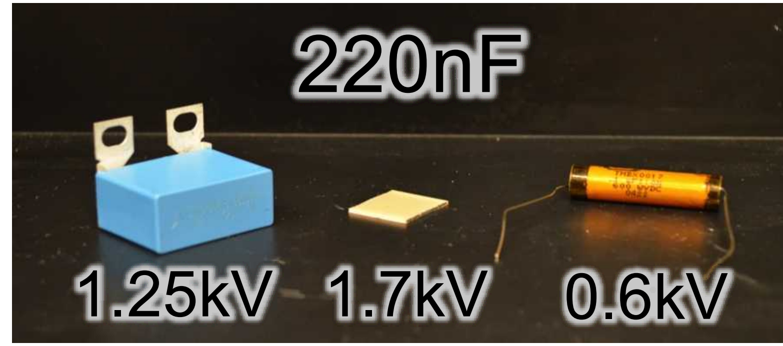




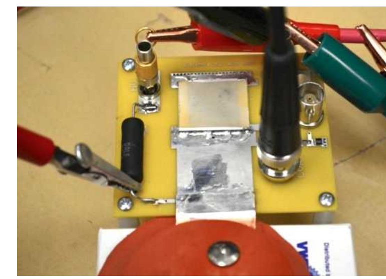
When the system requirements are well defined, we can develop capacitors from the compositional level to the component level to meet device requirements

Summary

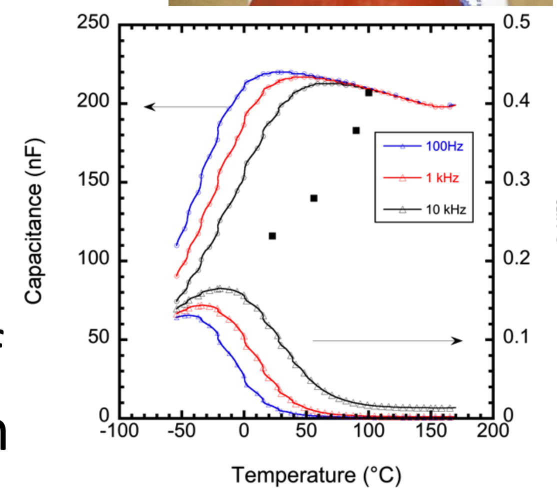
- 200 nF MLCCs were successfully fabricated from BZT-80BT



- Core-shell structures were identified as possible contributors to reduced field tuning



- Capacitance values calculated from pulse discharge data reveals that the dielectric relaxation is observable in the time domain



- We are working to reduce the temperature of the dielectric relaxation through solid solution formation

Acknowledgements

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- Jon Ihlefeld

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  - Dr. Imre Gyuk and the Department of Energy’s Office of Electricity Delivery and Energy Reliability

Questions?

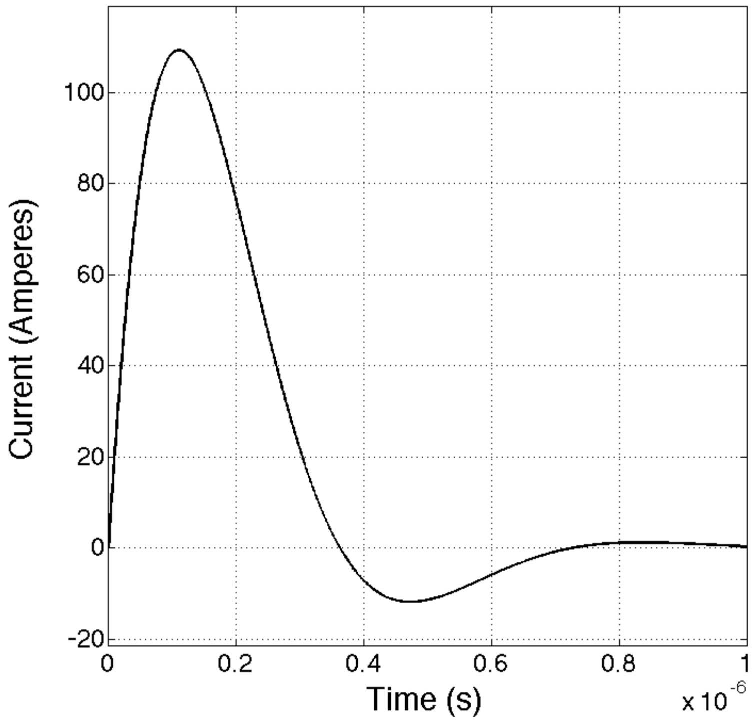
Harlan Brown-Shaklee
hjbrown@sandia.gov

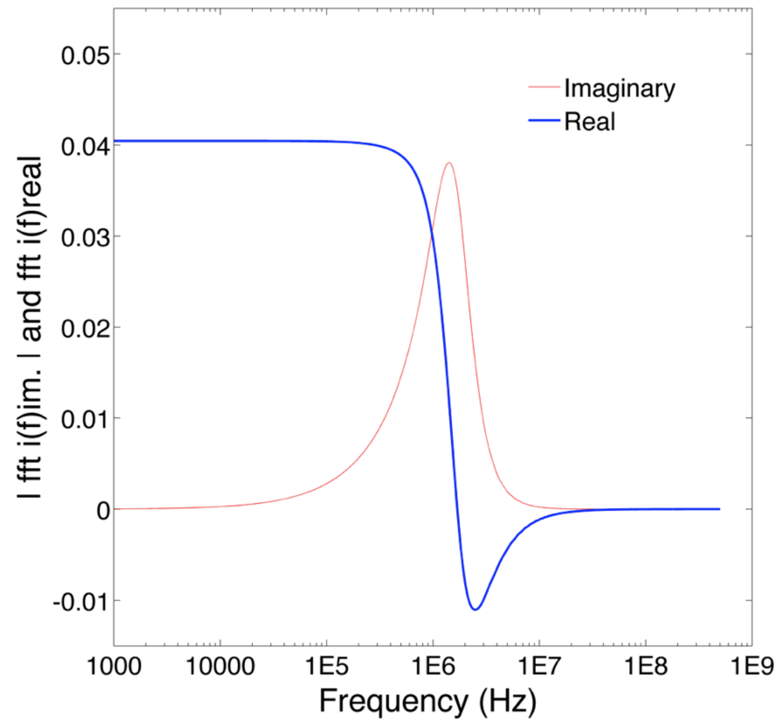
Dominant frequencies from a current pulse can be extracted using a Fourier transform

Current Waveform from Underdamped RLC Circuit

Fourier Transform

~1.4 MHz





Time Domain

Frequency Domain

Dominant frequency (~1.4MHz) of the current pulse measured with a CVR agrees well with that calculated from $\omega_0=2\pi f$