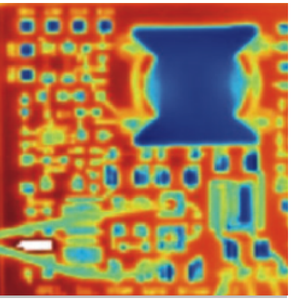
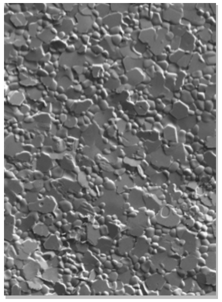
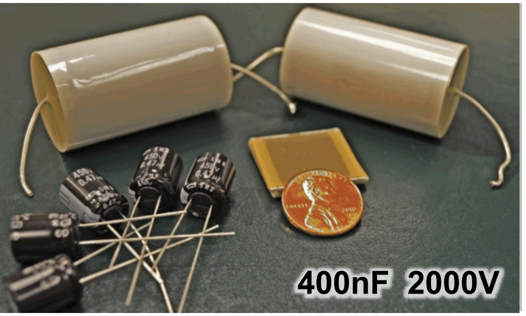

Sandia National Laboratories

Exceptional service in the national interest

SAND2014-1896C

Ceramic Capacitors for Applications Requiring High Reliability under Challenging Operating Conditions

Geoff Brennecka

Sandia National Laboratories

The author gratefully acknowledges the support of Dr. Imre Gyuk and the Department of Energy's Office of Electricity Delivery and Energy Reliability.

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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  - Prof. Brady Gibbons (OSU)
  - Yu Hong Jeon (OSU)
  - Chris Shelton (OSU, NCSU)
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  - Narit Triamnak (OSU)
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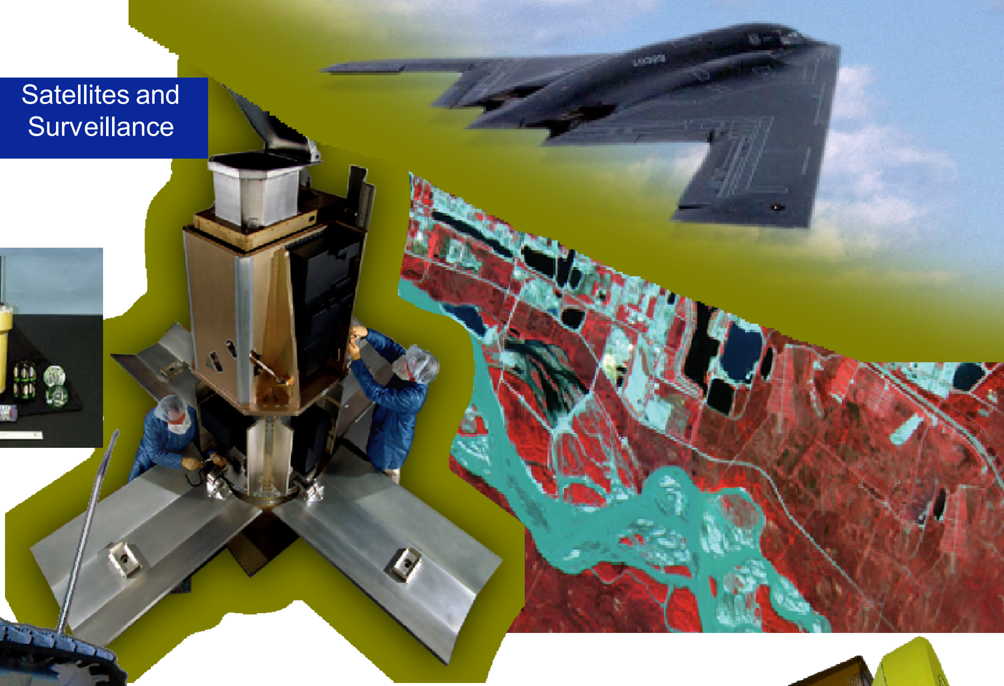
  - Kevin Ring (NM Tech)
  - Prof. Ian Reaney (Sheffield)
  - Prof. Wayne Huebner (MO S&T)
  - David Shahin (MO S&T, UMD)
  - Ryan Wilkerson (MO S&T, Berkeley)

Sandia's Work



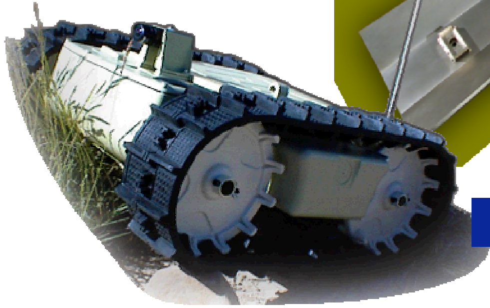
Satellites and Surveillance

Shuttle Orbital Inspection System

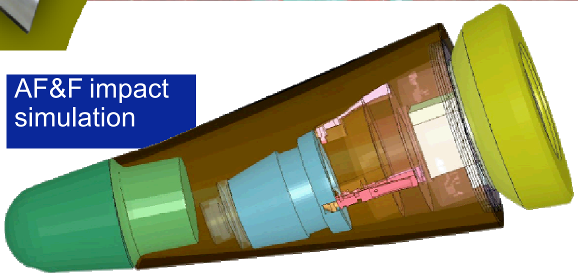
96% of total NW parts

UGS

Predator UAV with SAR

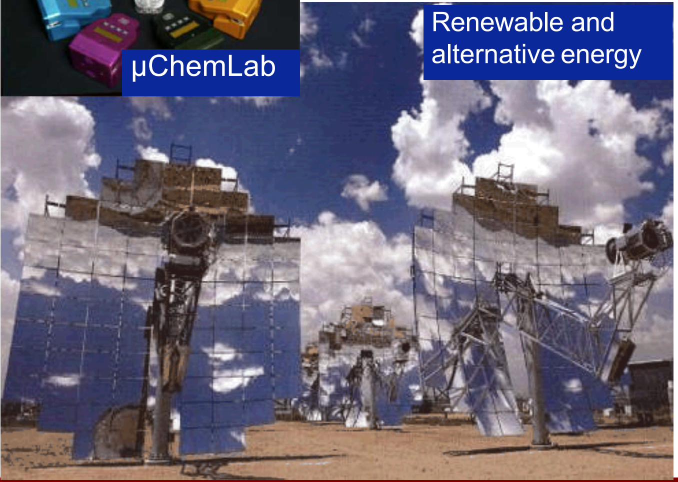


Robotics

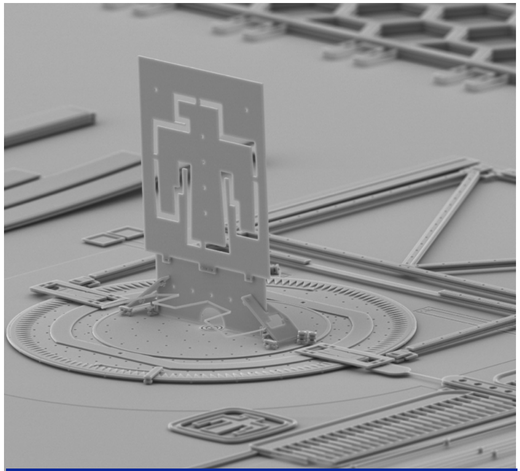


AF&F impact simulation

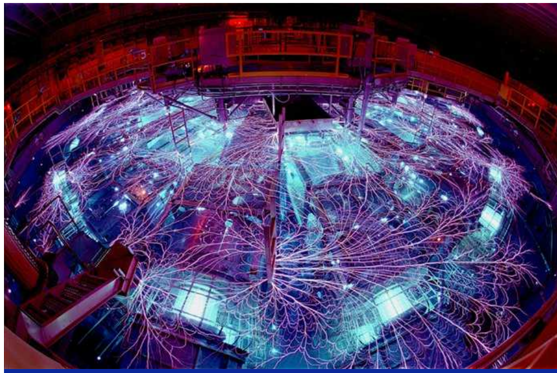
µChemLab



Renewable and alternative energy

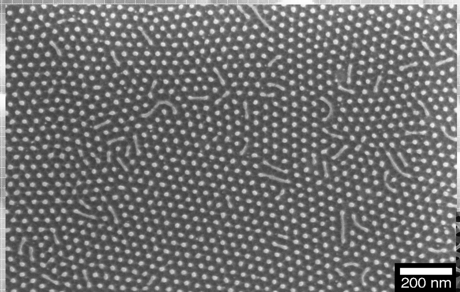


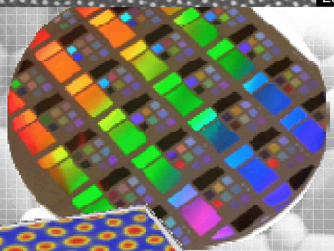
Clean room invented at SNL in 1963

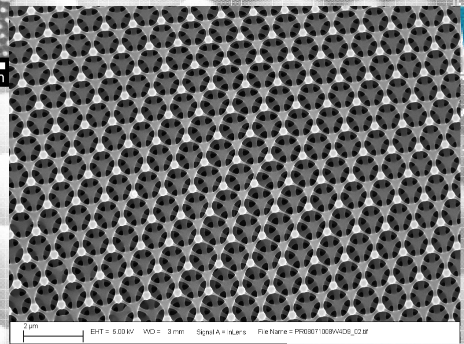


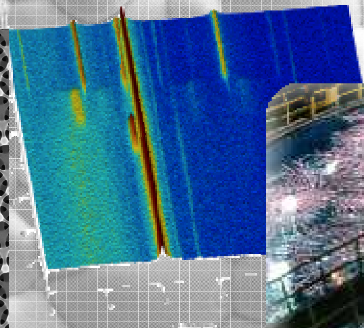
Z machine:
the world's most powerful X-ray source

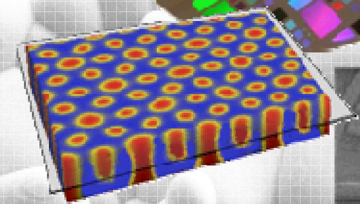
Our Projects…

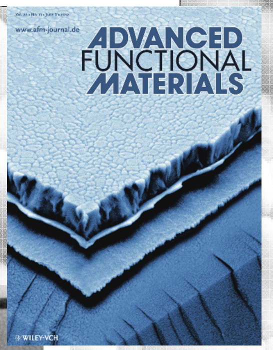


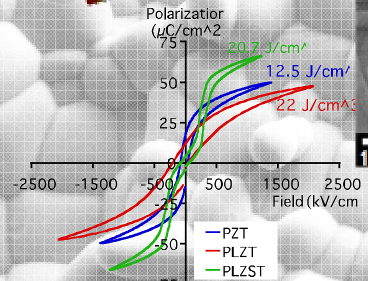


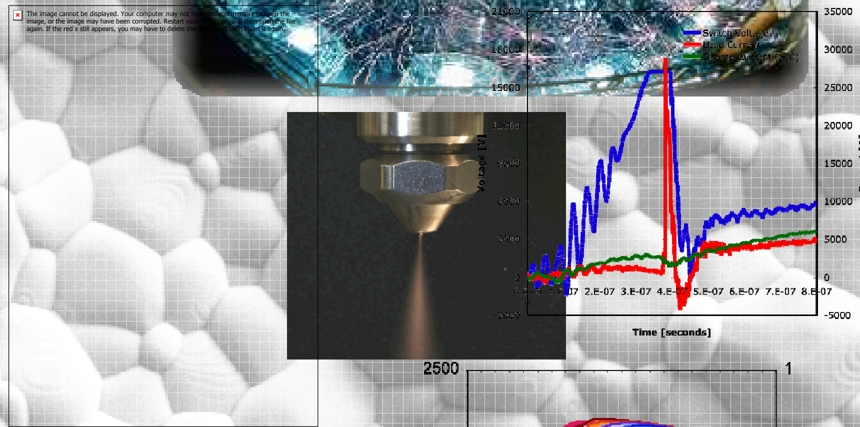


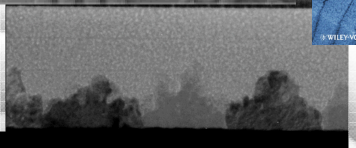


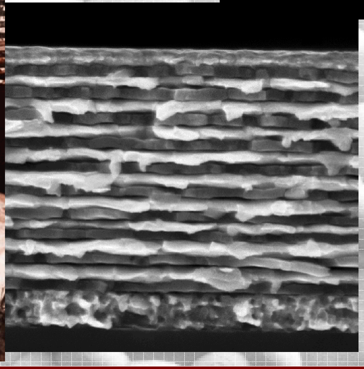


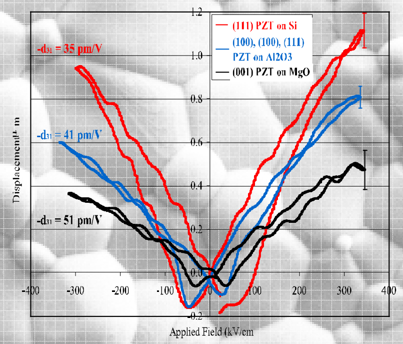


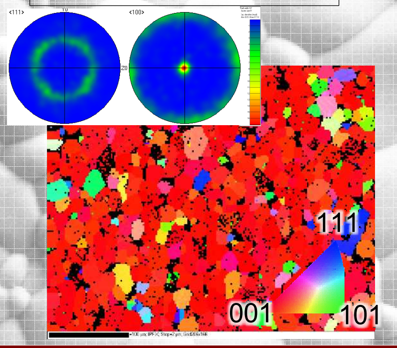


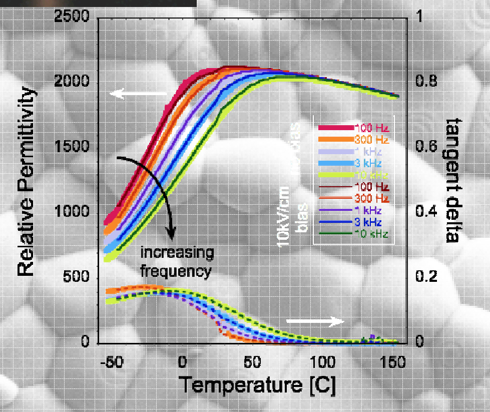


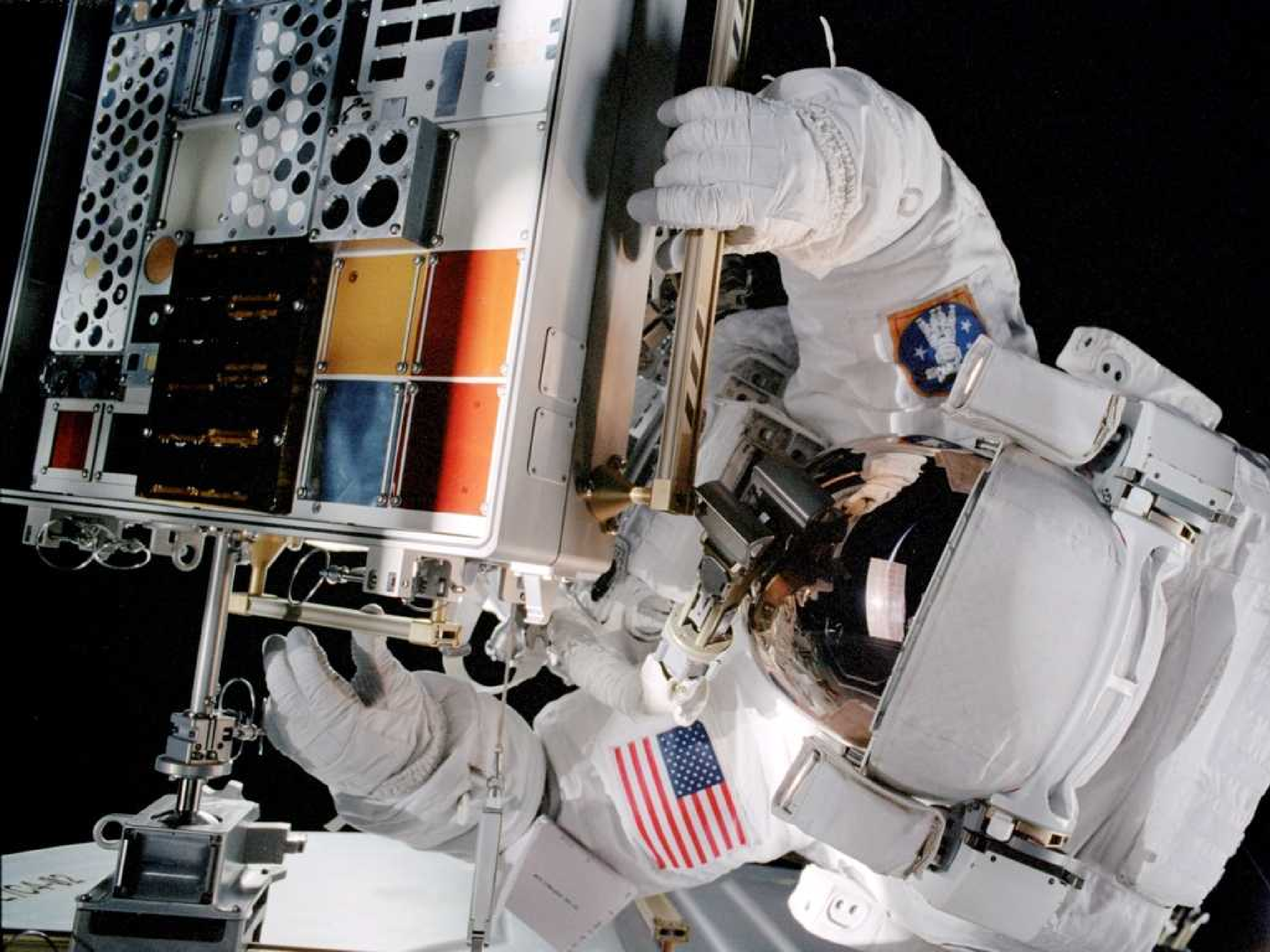












Outline

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- Application drivers:
  - High operating temperatures, high power: low ESR, low loss
  - Small volume: high energy density, low cost
  - Long life, reliable operation: high resistivity, high activation energy
- Material Performance
- Demonstration MLCC Fabrication
- Mechanisms
  - Structure
  - Microstructure
  - Processing
  - Defects

Combines batching, processing, thermo/phase, kinetics, defect chemistry, optical and electrical properties, relaxor physics, field response, characterization, etc.

Anatomy of a Typical Paper…

Sandia National Laboratories

INTRODUCTION

Capacitors are some sort of magical devices that are key to solving global warming[1], war[2-3], famine[4], and delayed flights[5-6]. Recently, other researchers have suggested that superduper capacitors may even be useful for buzzword[7] and another totally made up phrase[8]. My funding agency is especially fond of them because they have been funding this work for many years with nothing commercial to show for it, so these papers are how I justify continuing the gravy train[9-12]. Smith and Jones have also published in this area; I disagree with their conclusions, but I'm citing their papers because that's the first thing they'll look for if they review this.[13-16] The work from Andrews *et al.* is unrelated, but Tim will buy me a beer at the next conference if I cite him[17].

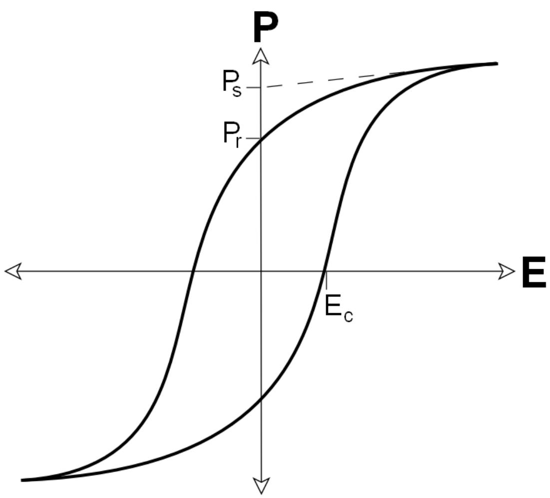
EXPERIMENTAL

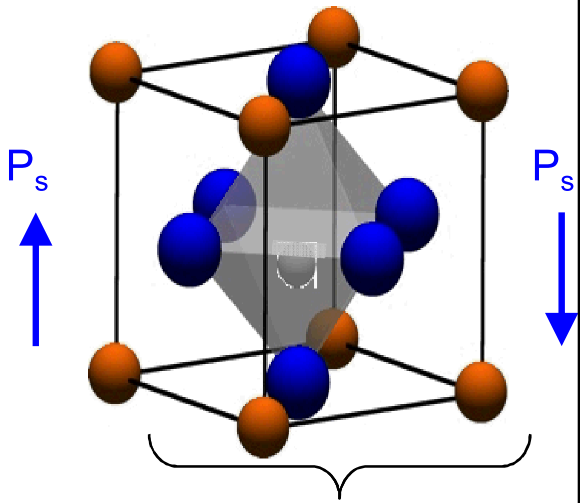
Parts were formed by typical ceramic methods. Processing is boring and doesn't matter anyway. Measurements were made using some home-built equipment that I don't understand and some commercial equipment that I *really* don't understand, so I pretend they're all black boxes that give me data I like.

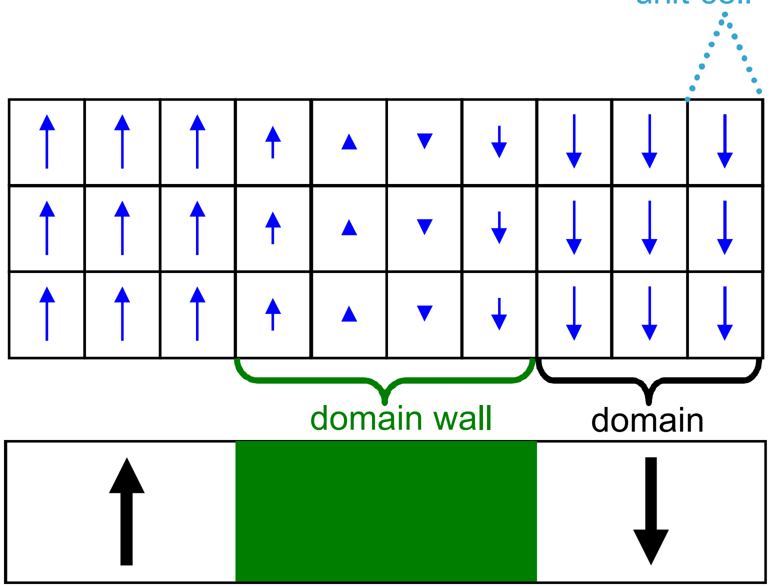
RESULTS

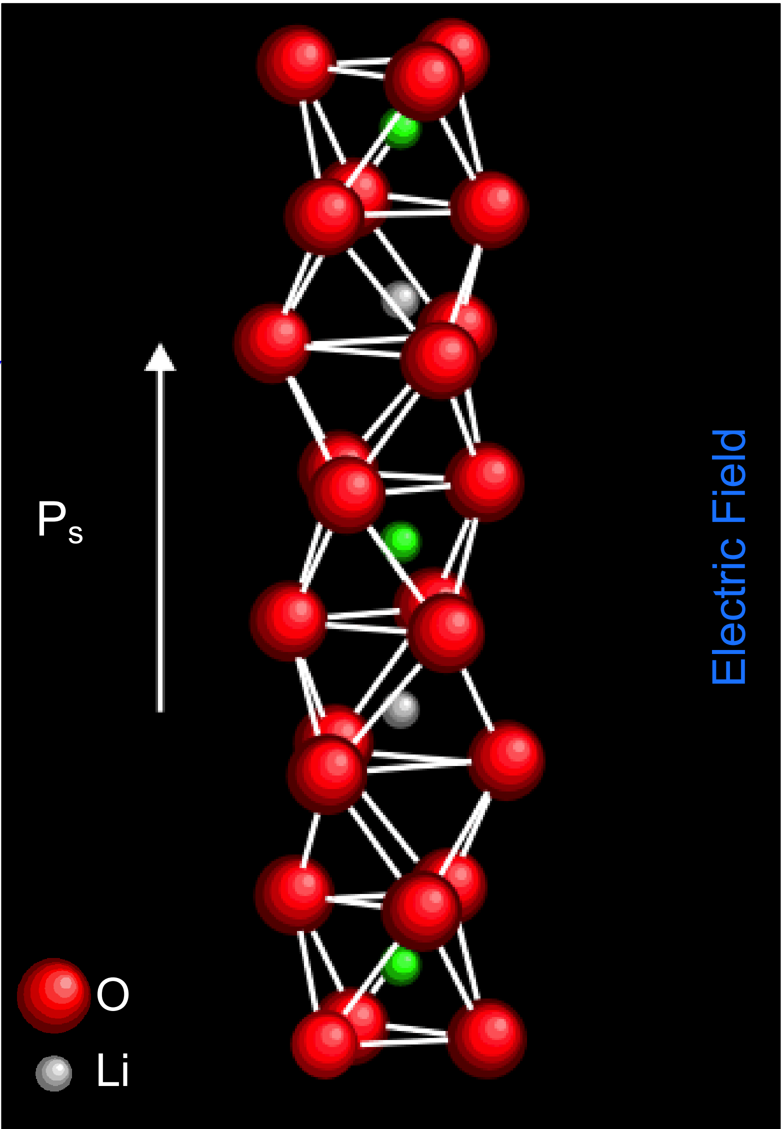
Here's some data. We don't know what it means, but we hope that you're just looking at the figures and title anyway. In fact, it's probably better if you don't pore over every last word of this manuscript. It is readily apparent from the small shoulder on the XRD peak in Fig 1 that we have formed the world's first spontaneous ultralattice. We didn't do any other characterization because it's expensive and slow and never tells us what we want to hear. In Fig 2 we show capacitance data; our instrument gave us other numbers too, but they were weird, so we ignored them…

Ferroelectrics









Animation courtesy of David Scrymgeour

Relaxor Ferroelectrics

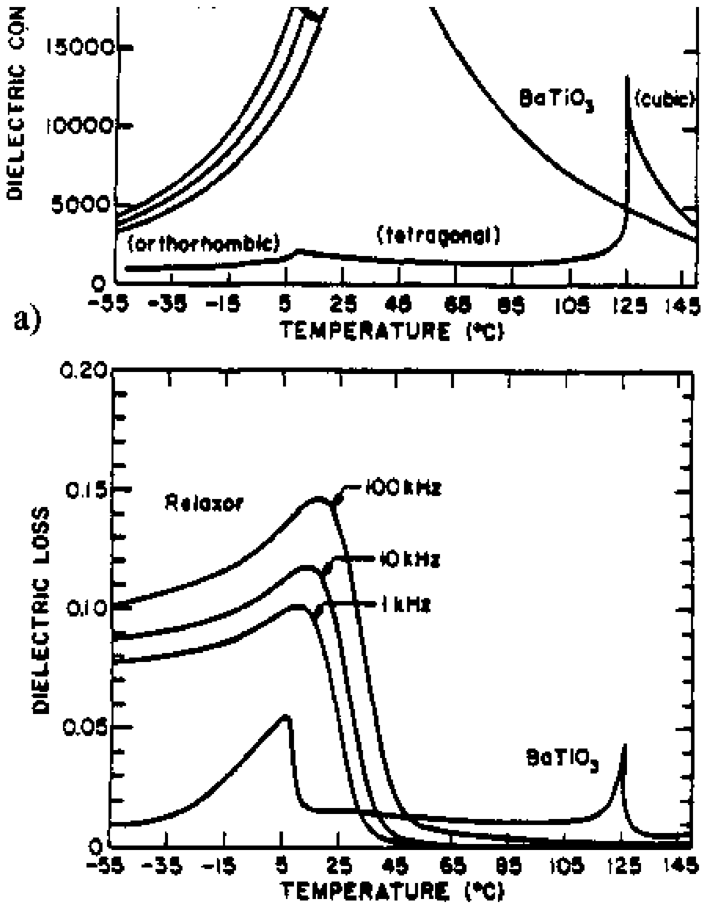
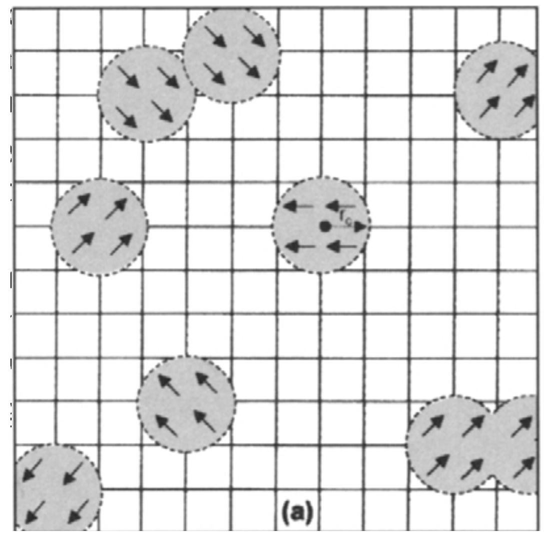
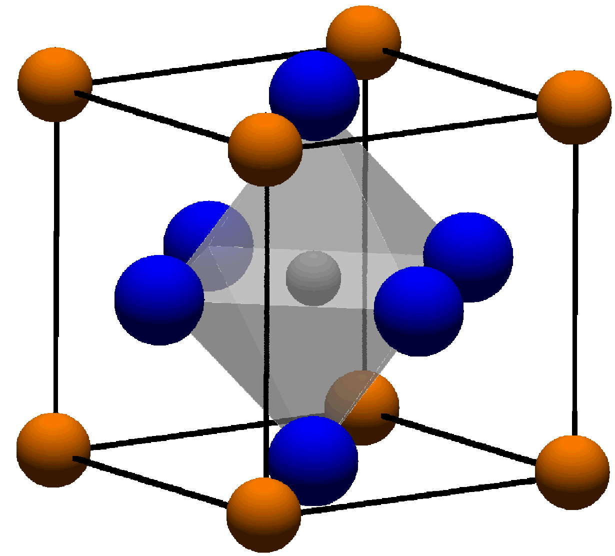


Table I. Property differences between

Shrout, ISAF 1990

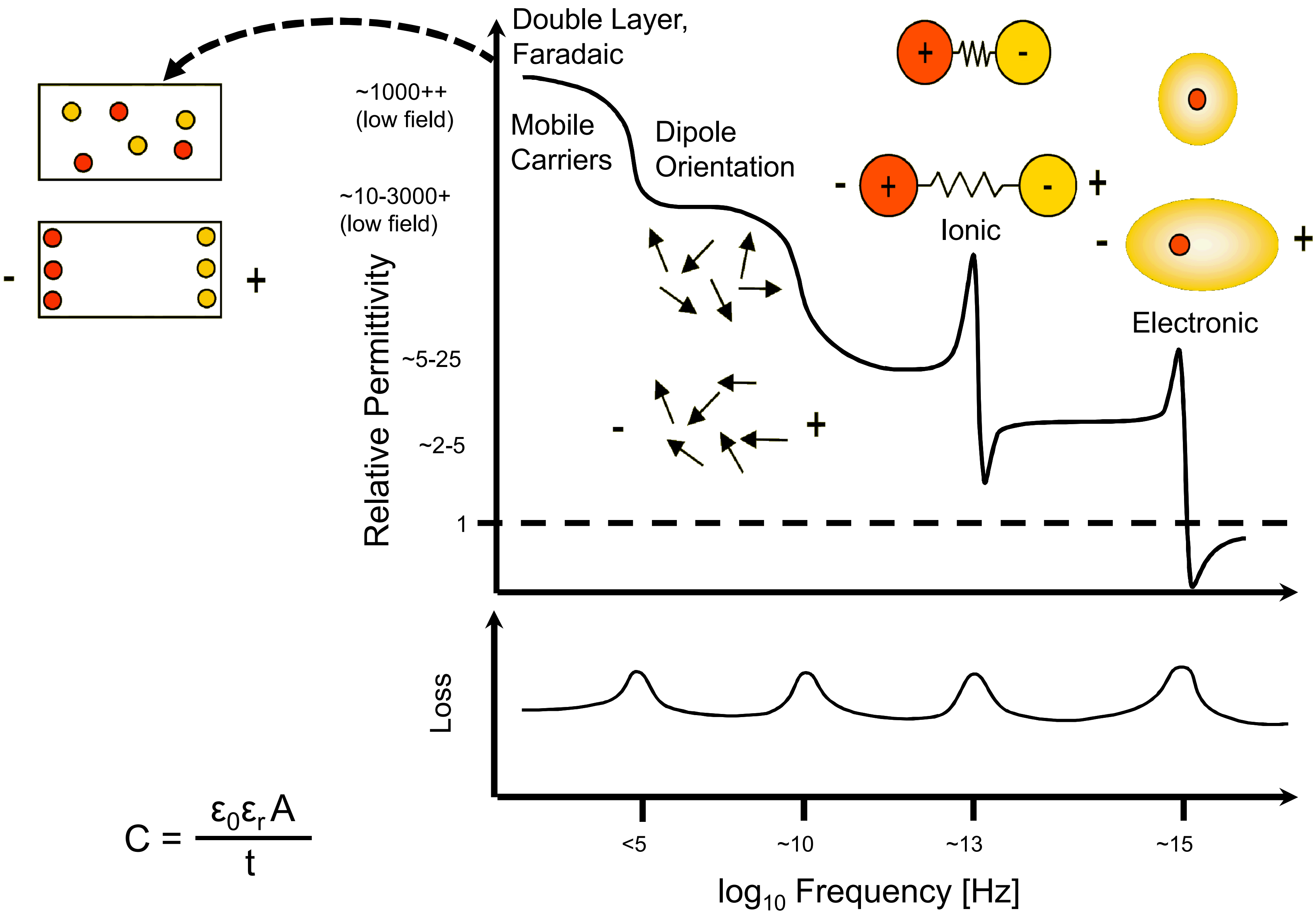


Samara, 2001



- Prototype is $Pb(Mg_{1/3}Nb_{2/3})O_3$
- Disorder (on B-site) and highly polarizable matrix lead to polar nanoregions
- Characteristic frequency dispersion in permittivity and loss maxima
- Dielectric response highly sensitive to pressure, electric field

Polarization Mechanisms



$$C = \frac{\varepsilon_0 \varepsilon_r A}{t}$$

Capacitors

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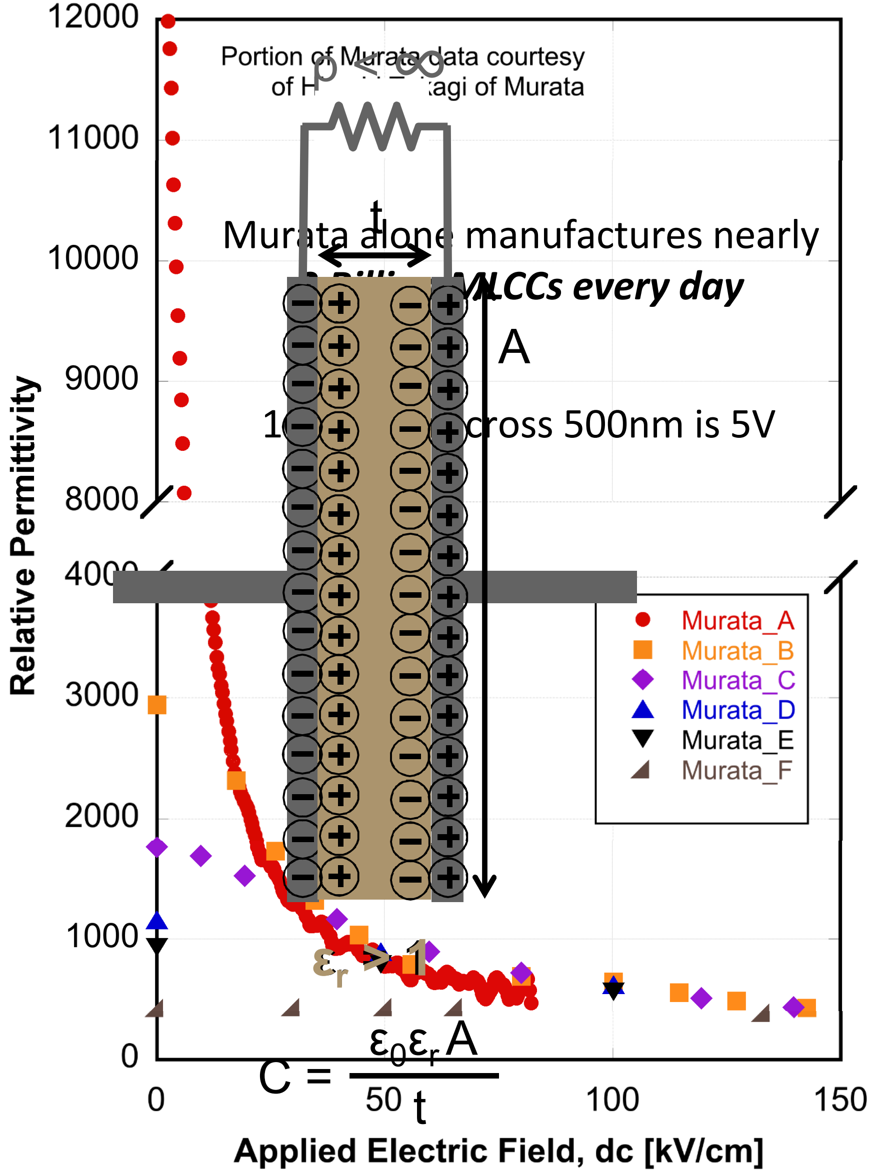
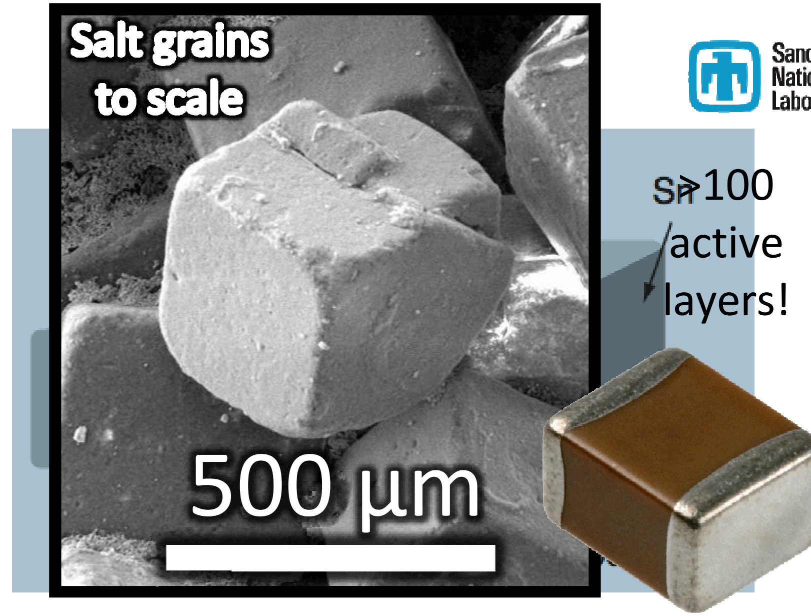
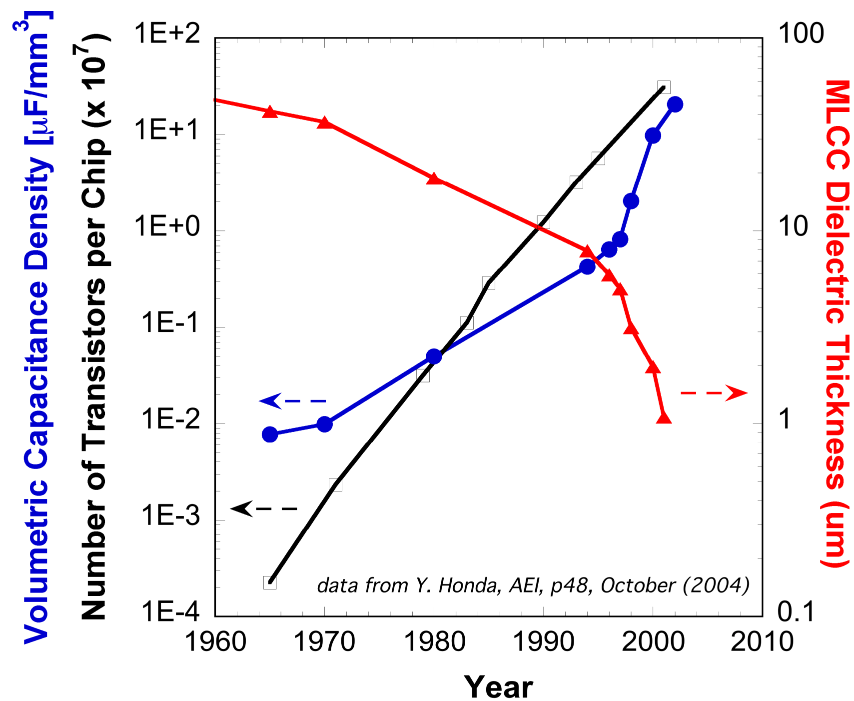
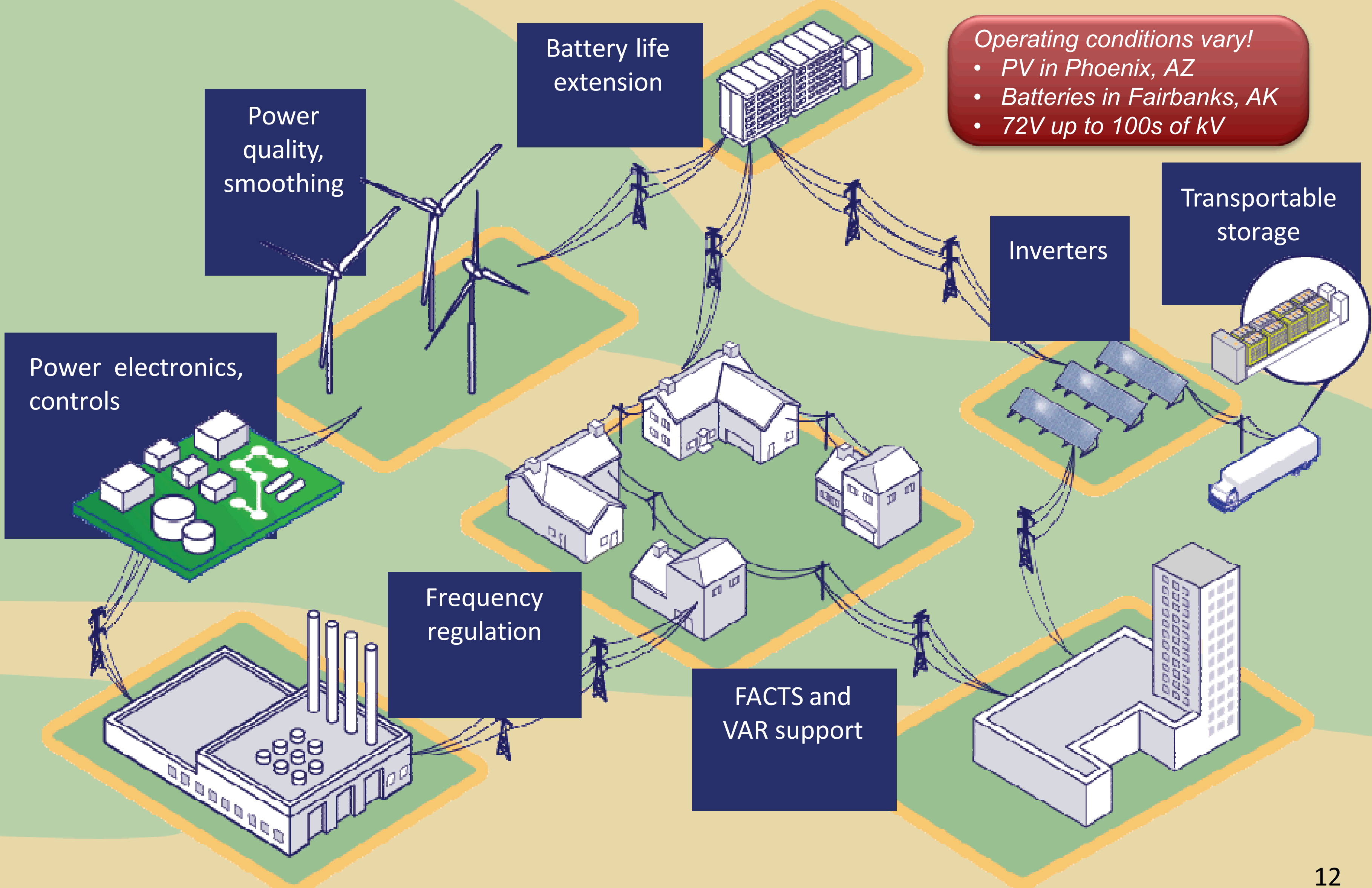




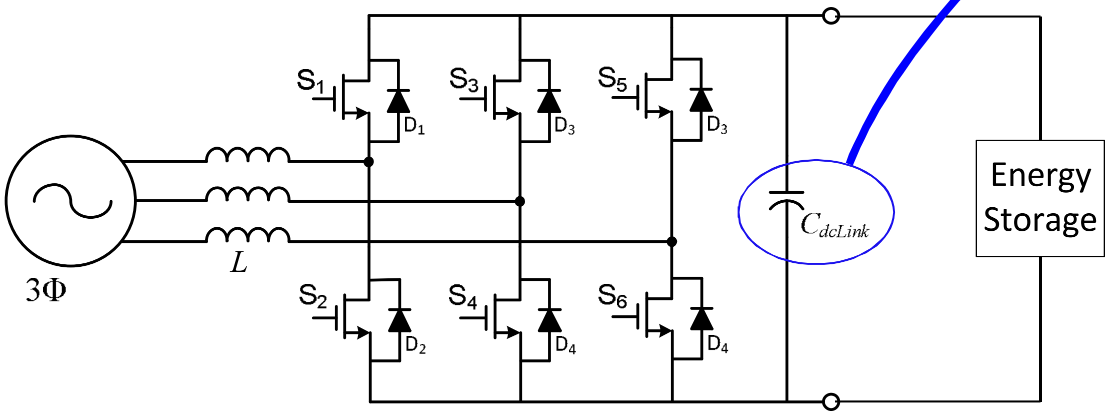


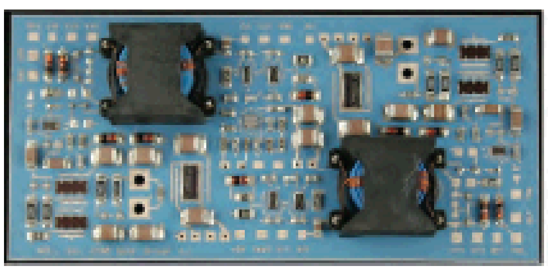
Capacitor Needs for Grid Storage

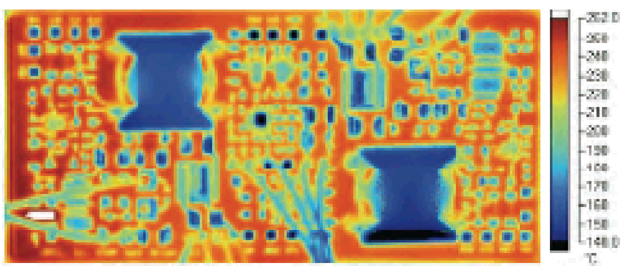


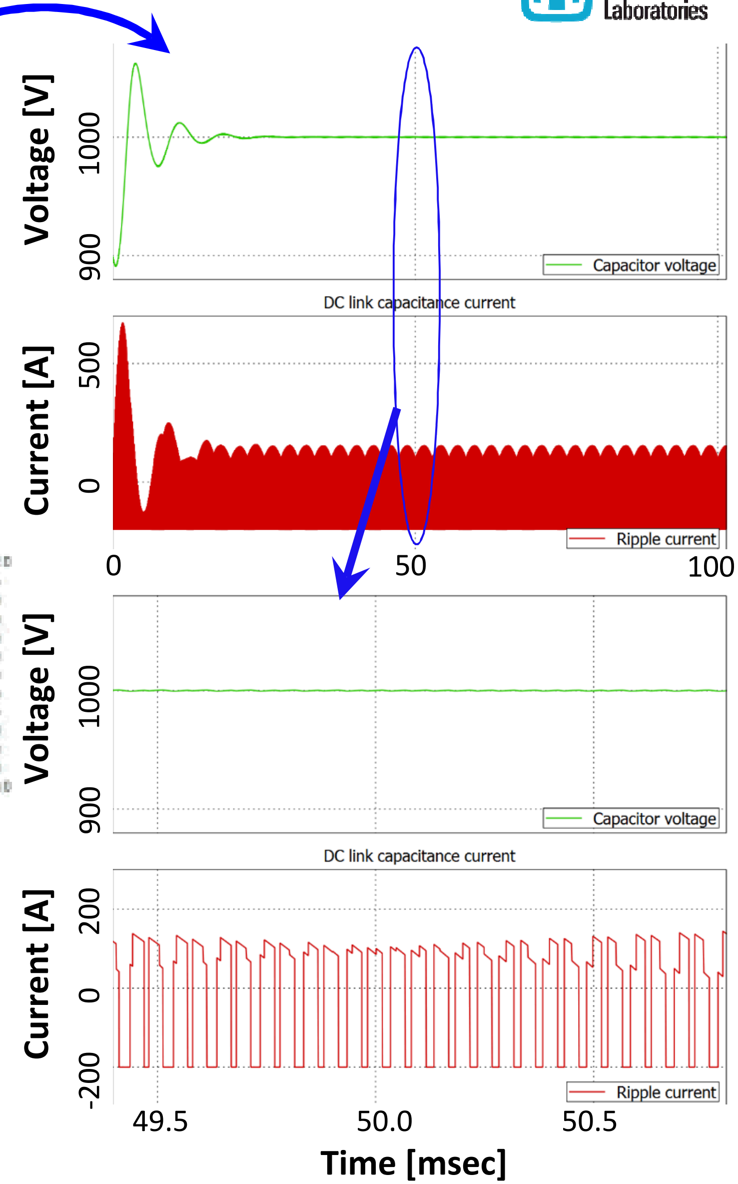
Geoff Brennecka, Sandia National Laboratories

Application Space



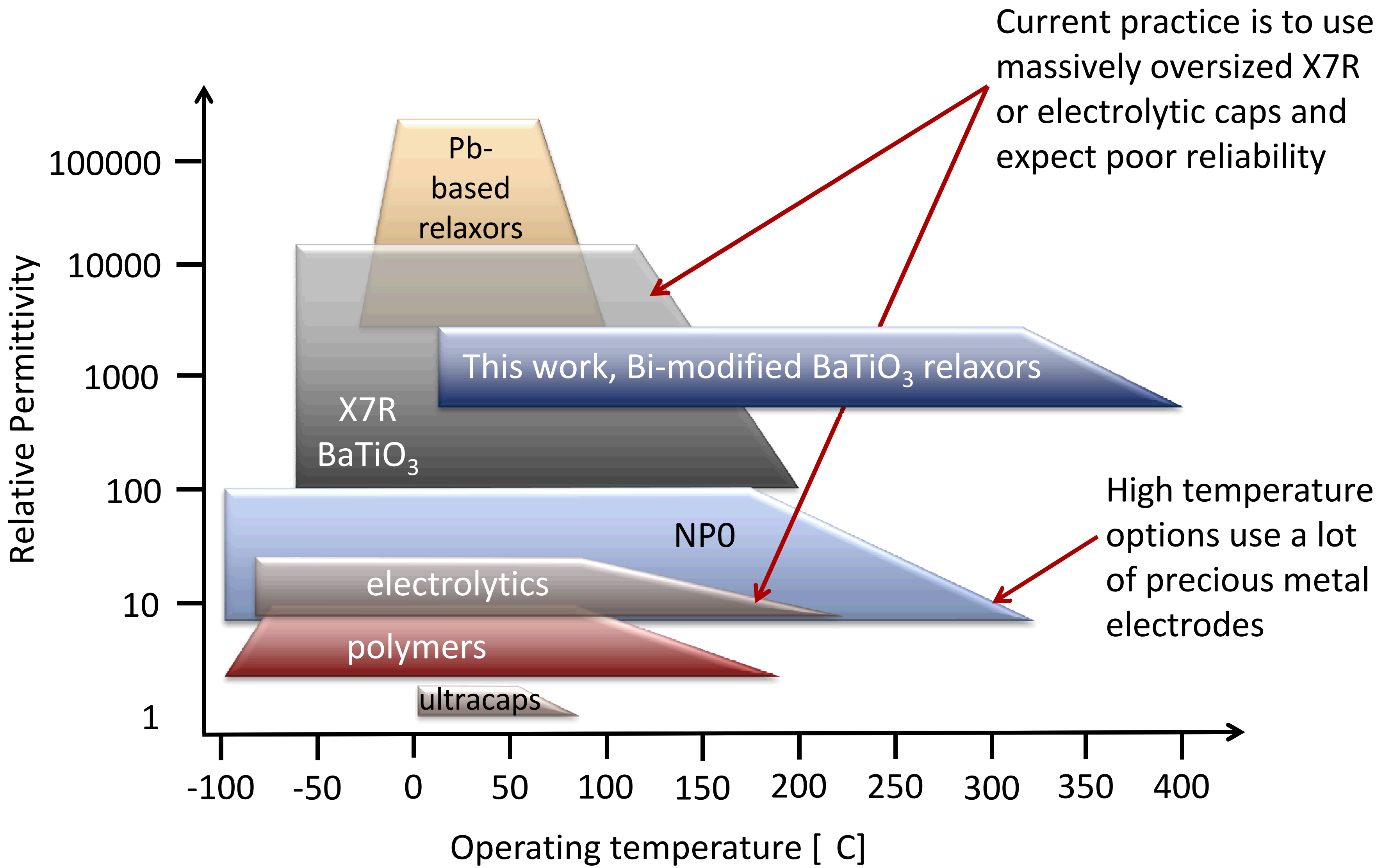






- High energy density, high capacitance density
- Operation >200°C needed, >300°C desired
- Low ESR for ripple current and power handling
- Decades of reliable operation

Available Options

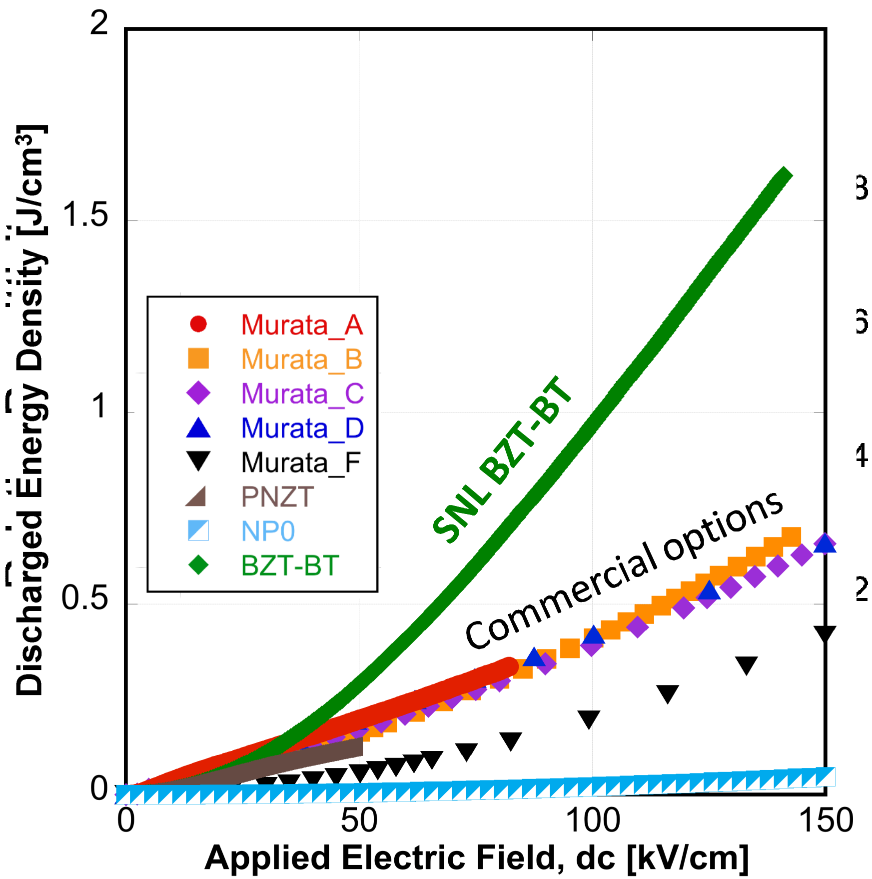


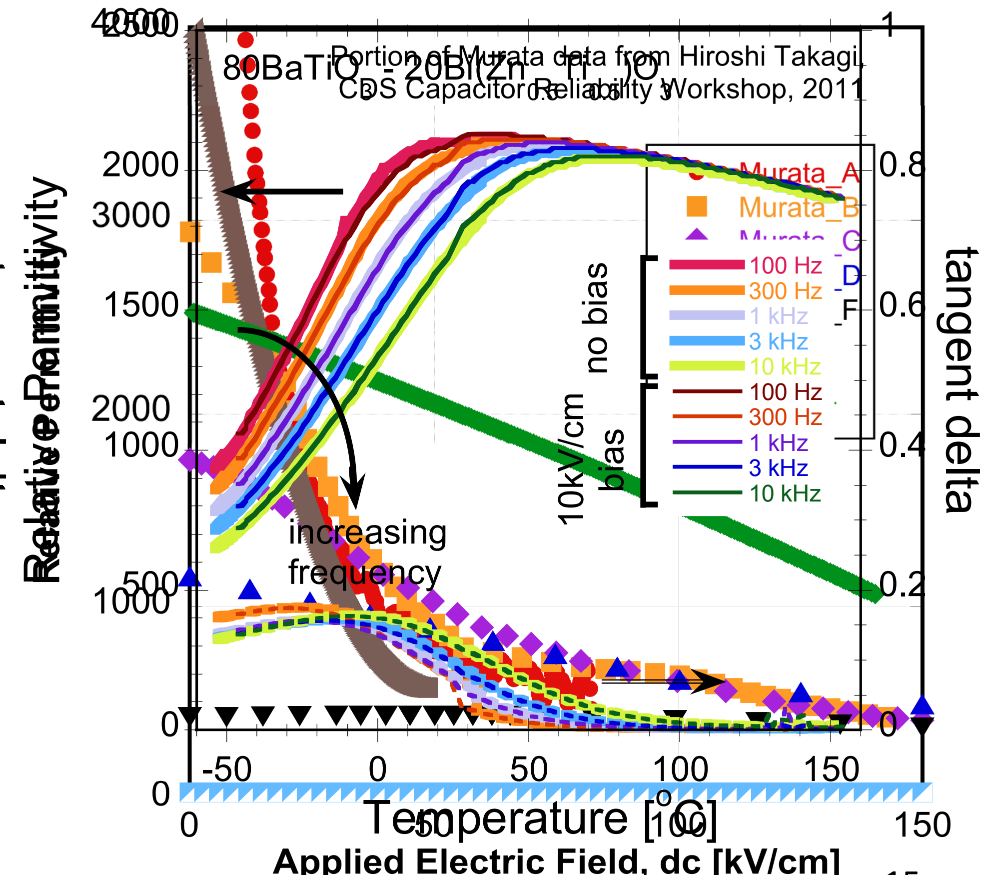
High Energy Density Dielectrics

$$J = \int_0^{V_{max}} CV^2 \rightarrow \int_0^{E_{max}} KE^2$$

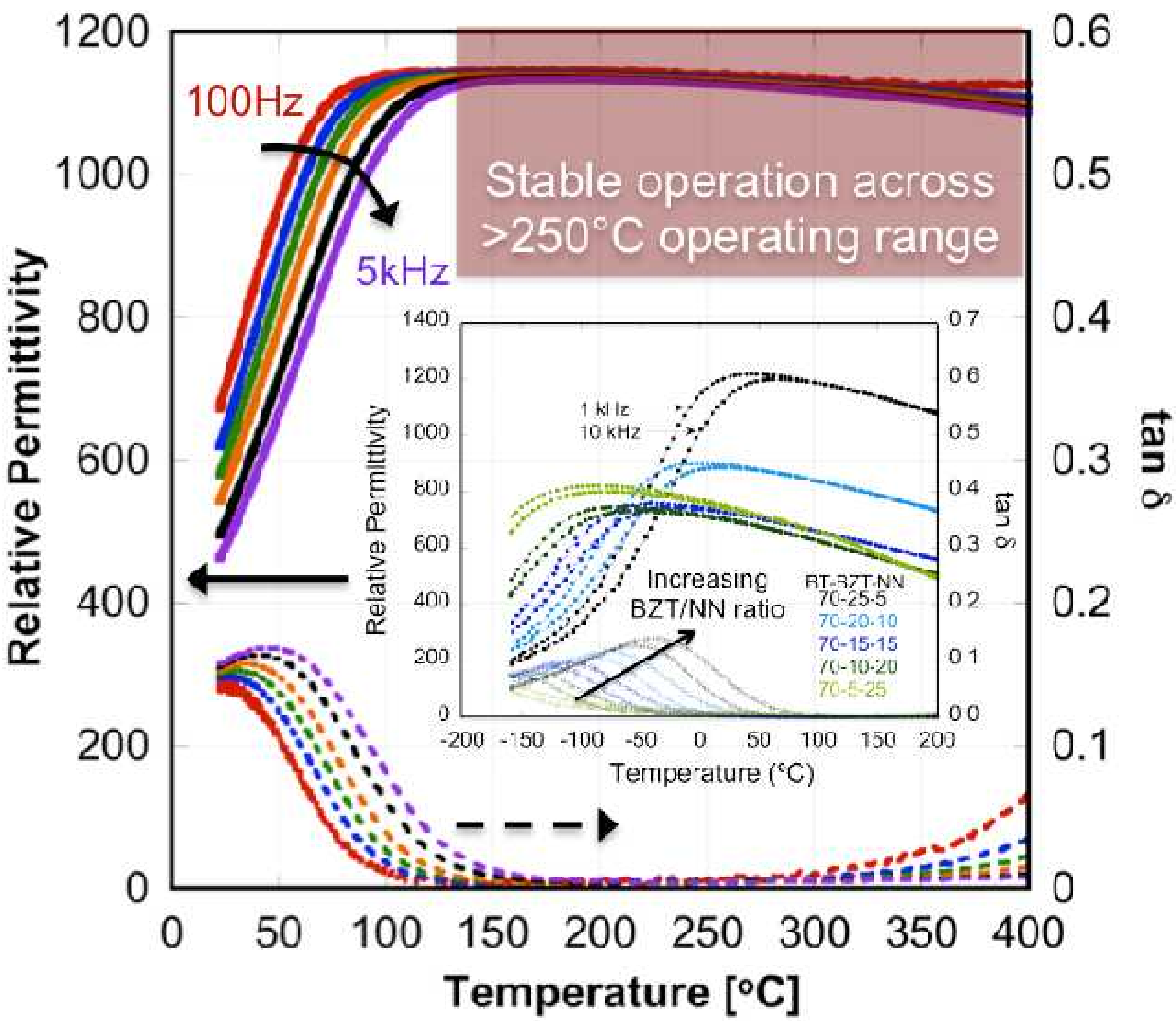
For high-K materials, K=K(E)

→ maintaining high K at high E is important





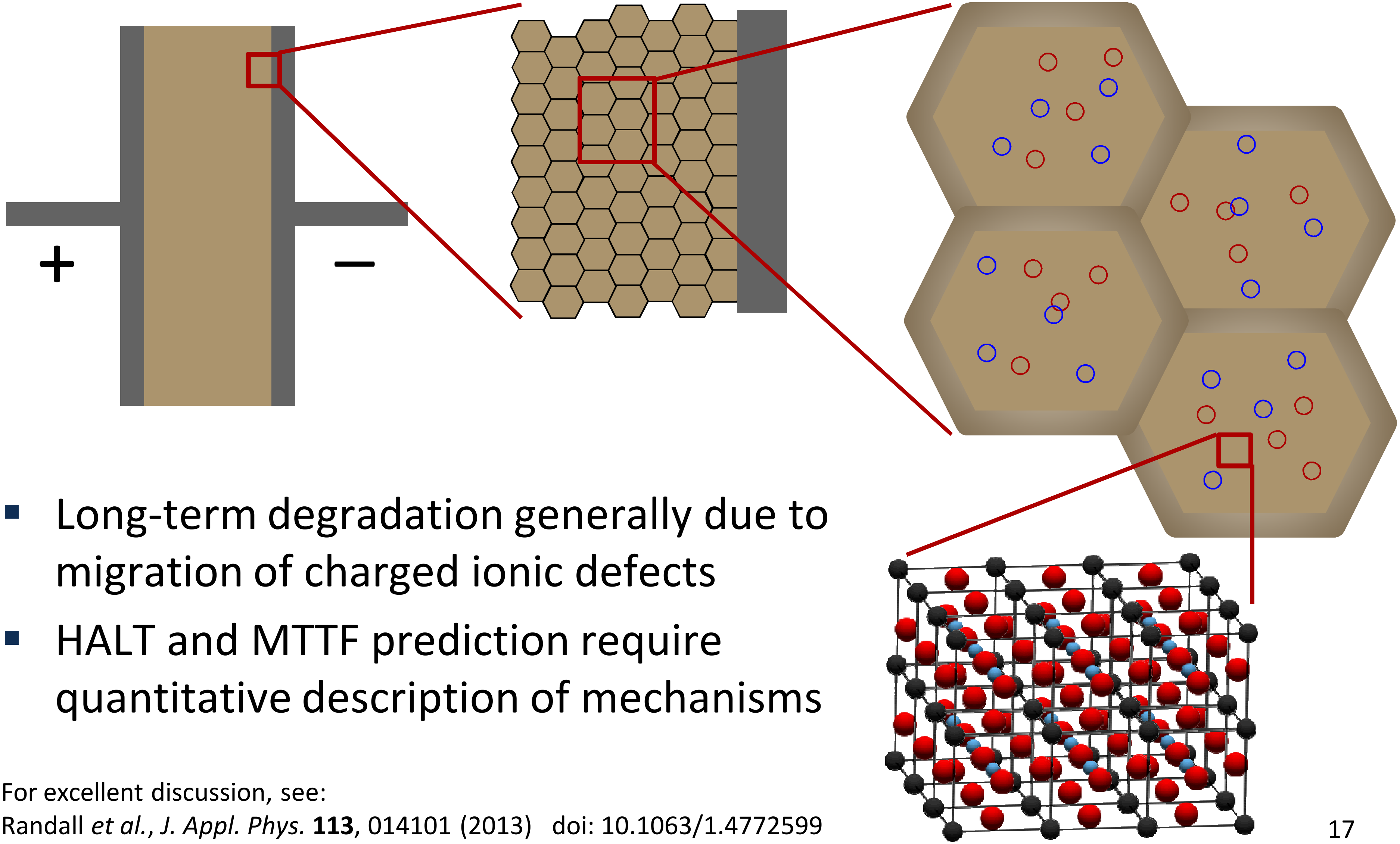
High Temperature Operation



- $BiScO_3$ stabilizes high temperature permittivity
- $SrTiO_3$ or $NaNbO_3$ additions shift relaxor transition to lower temperatures

We can shift the temperature range for stable operation around by ~250°C via chemical modification *without sacrificing voltage stability*

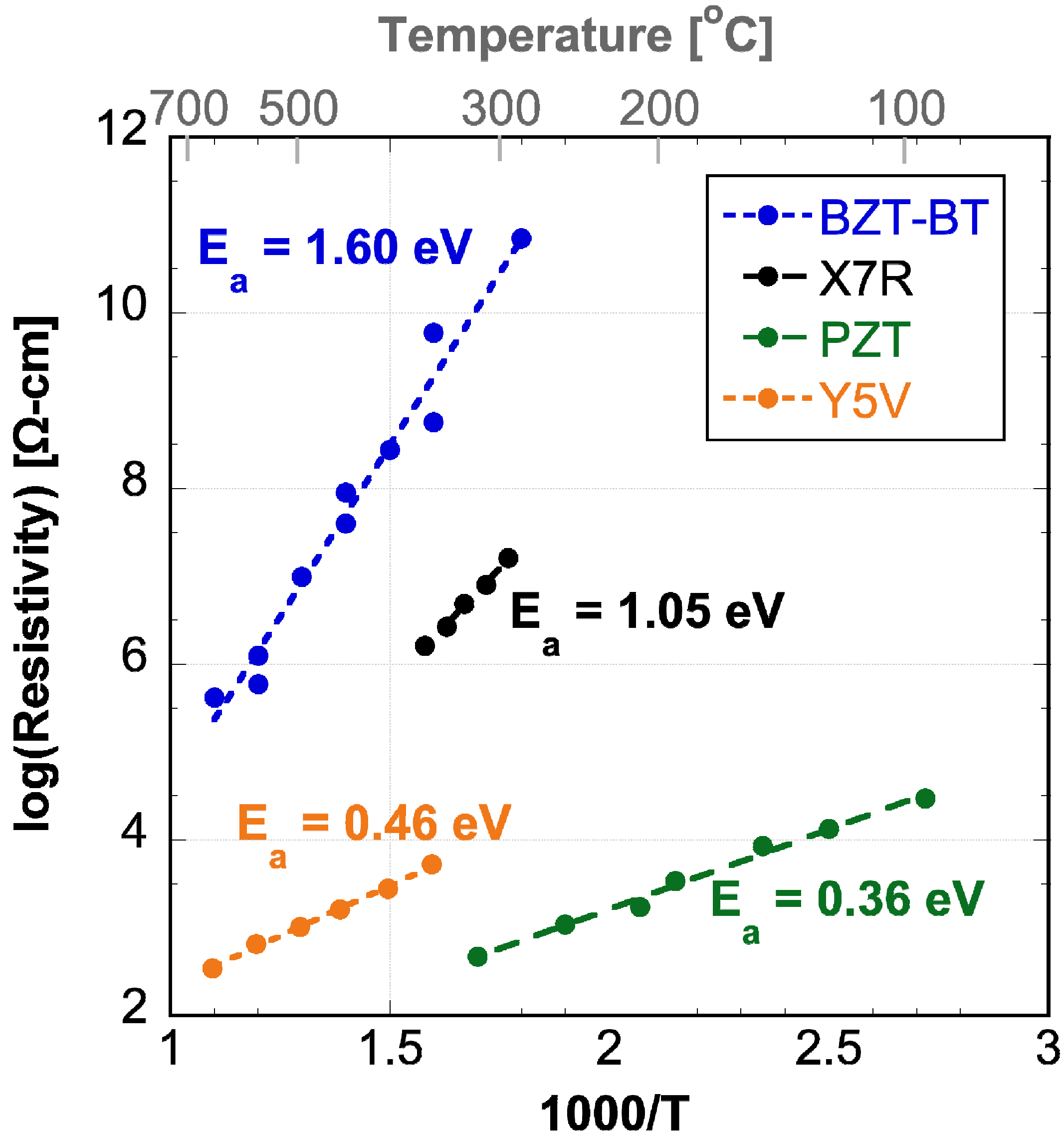
Degradation in Ceramic Dielectrics

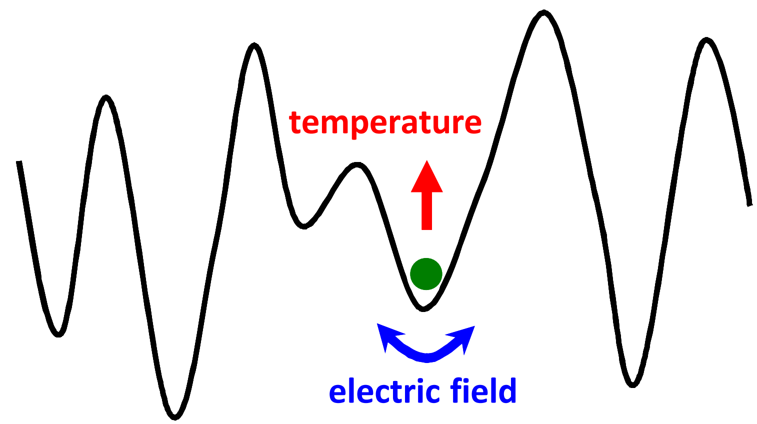


- Long-term degradation generally due to migration of charged ionic defects
- HALT and MTTF prediction require quantitative description of mechanisms

For excellent discussion, see:
Randall *et al.*, *J. Appl. Phys.* **113**, 014101 (2013) doi: 10.1063/1.4772599

High Resistivity → Reliable





Higher resistivity and larger activation energy for conduction both translate into longer lifetimes and higher reliability, particularly at elevated temperatures.

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  - Long life, reliable operation: high resistivity, high activation energy
- Material Performance
- Demonstration Fabrication
- Mechanisms
  - Structure
  - Microstructure
  - Processing
  - Defects

Prototype MLCCs: 200nF @ 1700V

$BaCO_3$	ZnO	Bi_2O_3	TiO_2

Mix/mill, calcine @ 950°C, Mill

Single phase by XRD

Prototype MLCCs: 200nF @ 1700V

$BaCO_3$	ZnO	Bi_2O_3	TiO_2

Mix/mill, calcine @ 950°C, Mill

Single phase by XRD

Bind, Press, Sinter @ 1120-1180°C

The image cannot be displayed. Your computer may not have enough memory to open the image, or the image may have been corrupted. Restart your computer, and then open the file again. If the red x still appears, you may have to delete the image and then insert it again.

Prototype MLCCs: 200nF @ 1700V

$BaCO_3$ | ZnO | Bi_2O_3 | TiO_2

Mix/mill, calcine @ 950°C, Mill

Single phase by XRD

Bind, Press, Sinter @ 1120-1180°C

Cast and co-fire with Pt @ 1120°C

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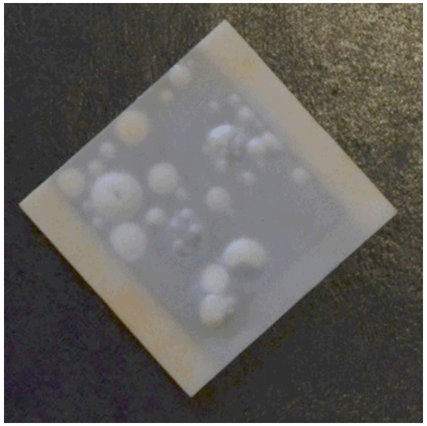

Prototype MLCCs: 200nF @ 1700V

MLCC Binder Burnout

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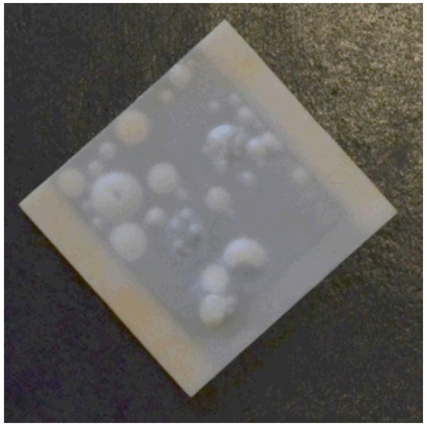
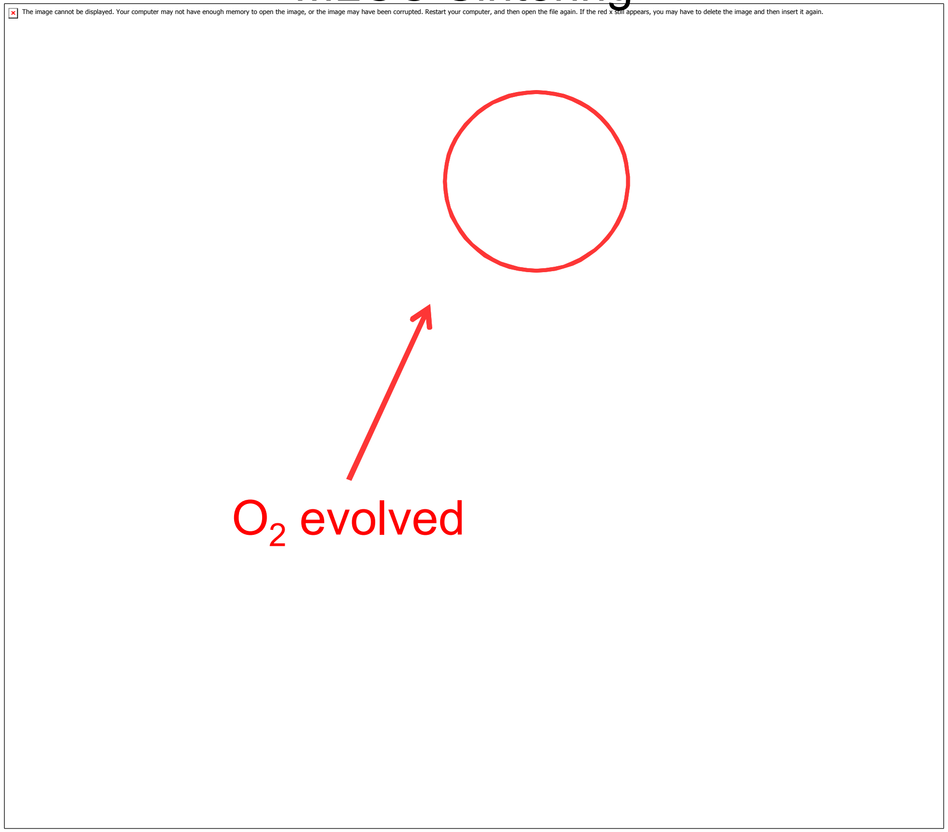
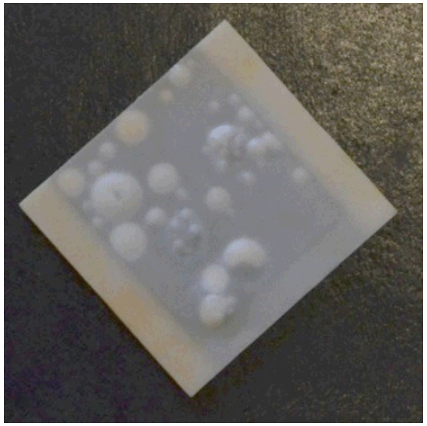


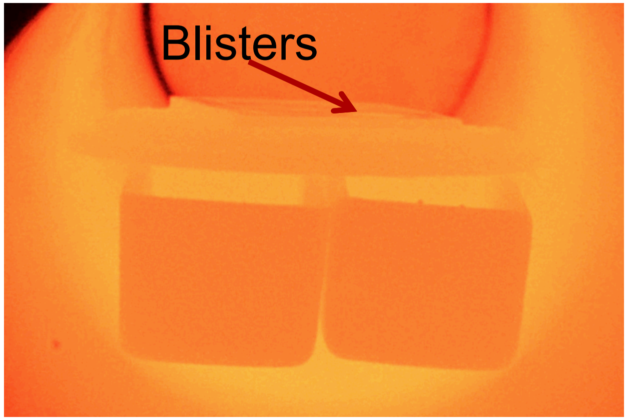
Prototype MLCCs: 200nF @ 1700V

MLCC Sintering



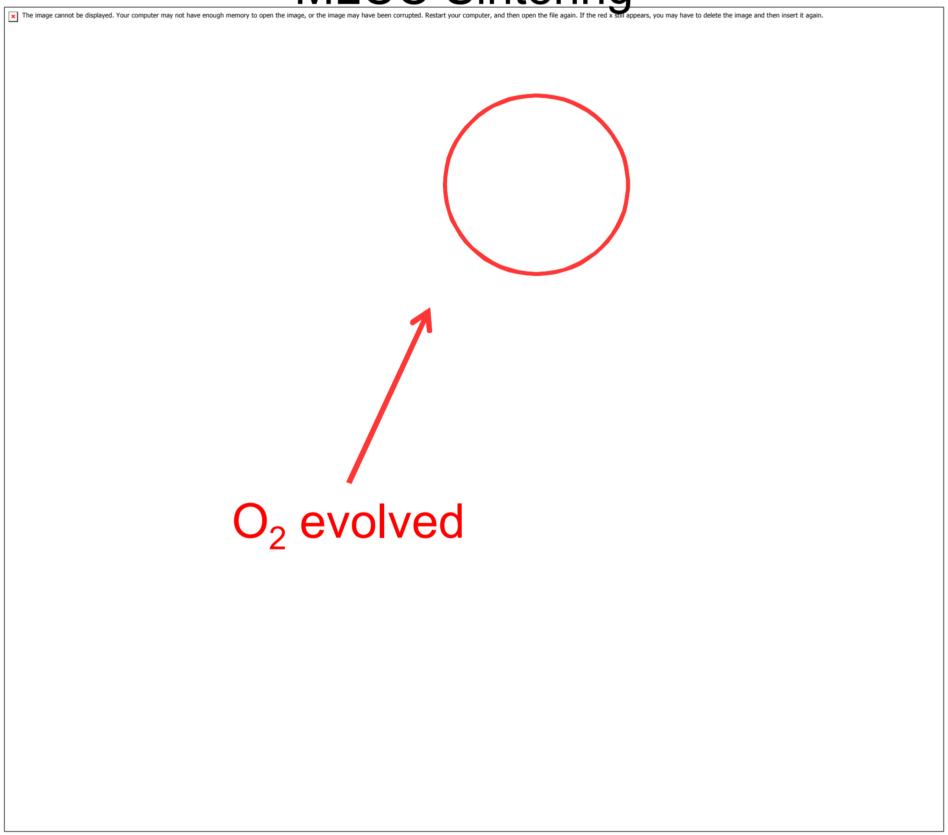


MLCC sintering at 1210°C



Prototype MLCCs: 200nF @ 1700V

MLCC Sintering



Cast and co-fire with Pt @ 1040°C

Prototype MLCCs: 200nF @ 1700V

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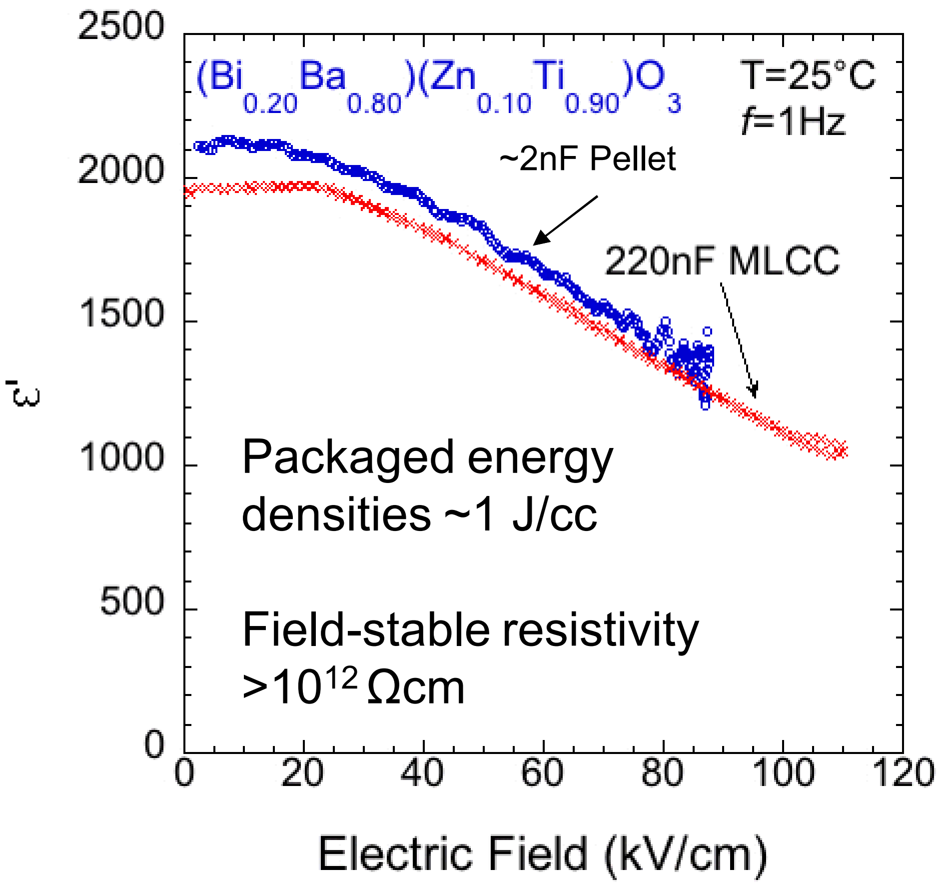
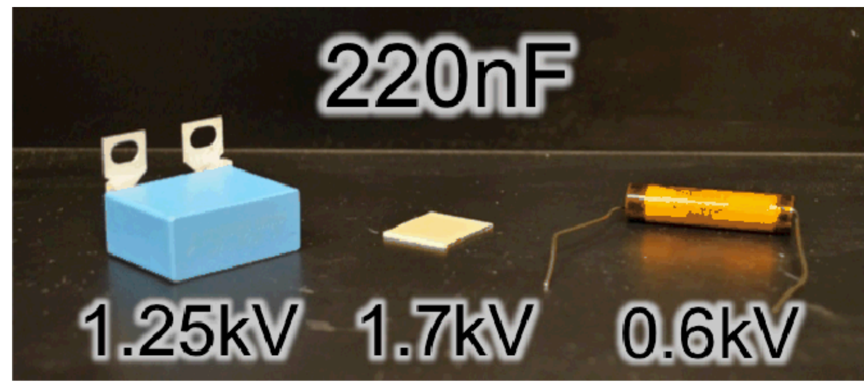
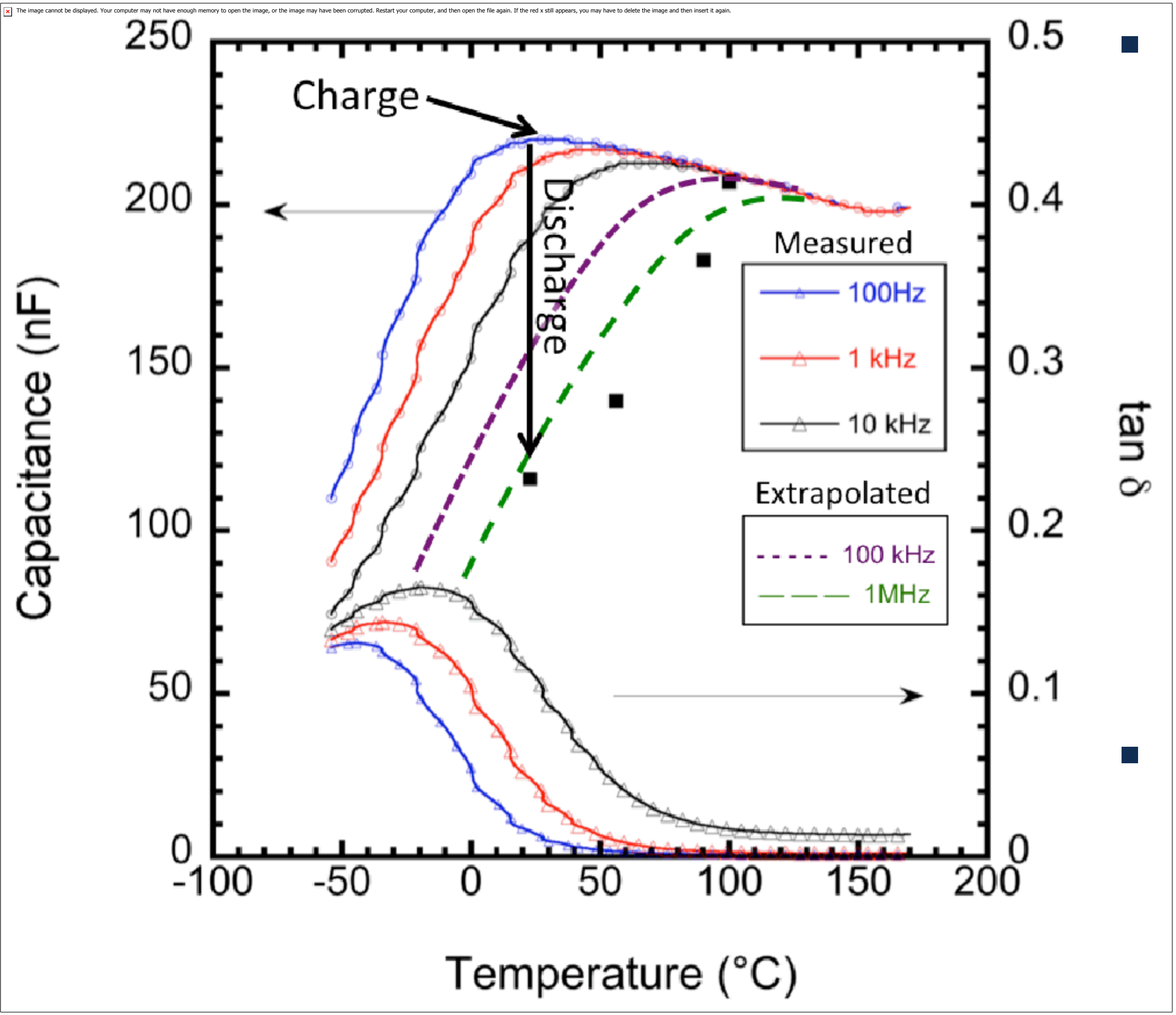


Cast and co-fire with Pt @ 1040°C



- Large MLCCs retain performance across operating temperatures, electric fields.
- Mechanism(s)??

Time Domain Performance



- Relaxor dielectrics exhibit characteristic frequency dispersion over relatively broad temperature ranges
  - For switched inverter designs which charge slowly and discharge quickly at irregular intervals, which values are relevant?
- Direct time-domain measurements map well to frequency domain data

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  - Processing
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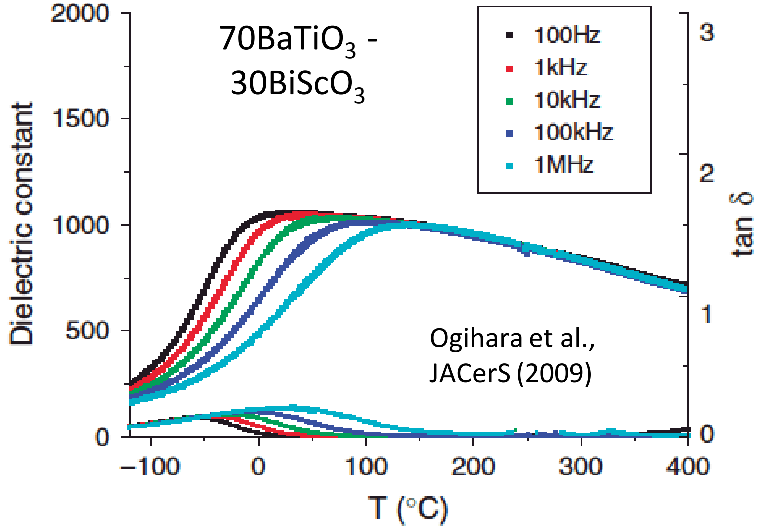
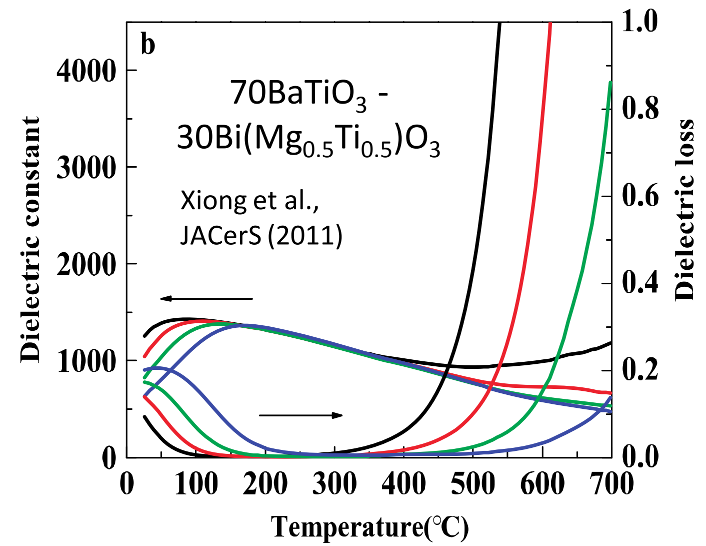
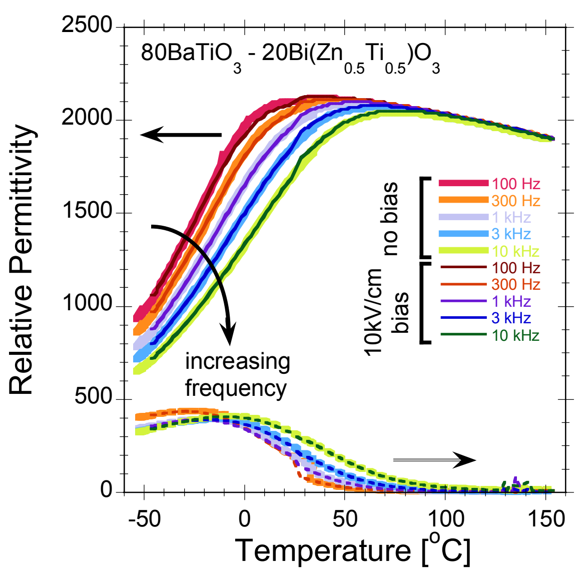
Bi-modified $BaTiO_3$ Relaxors

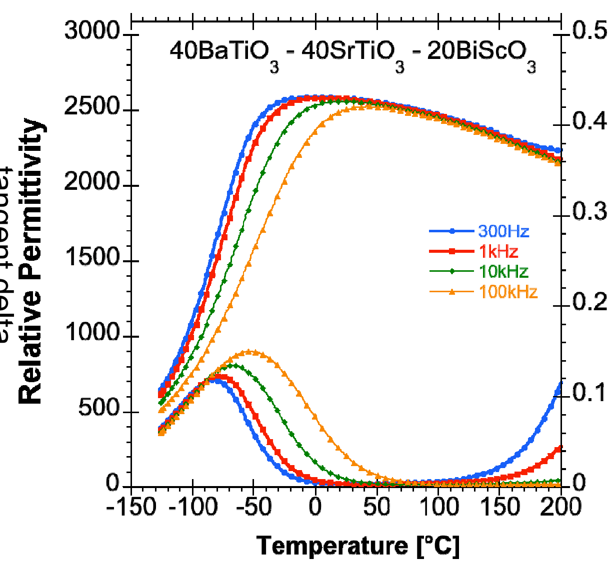
$BaTiO_3$ +

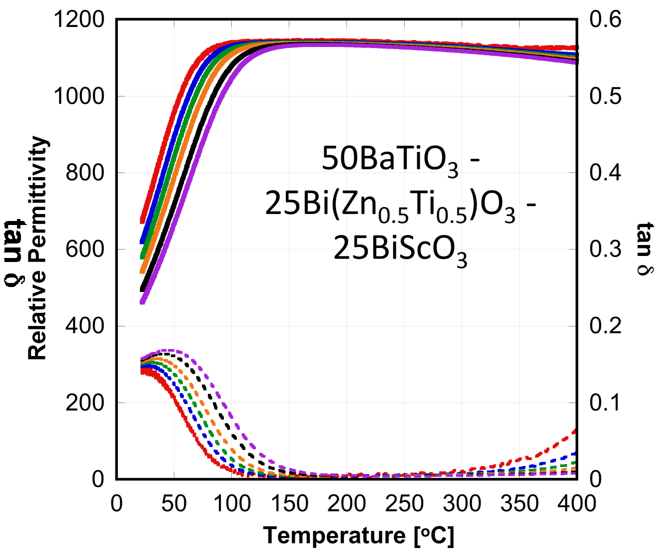
- $Bi(Zn_{0.5}Ti_{0.5})O_3$
- $Bi(Mg_{0.5}Ti_{0.5})O_3$
- $BiScO_3$
- $BiFeO_3$
- $BiInO_3$
- $Bi(Ni_{0.5}Ti_{0.5})O_3$
- …



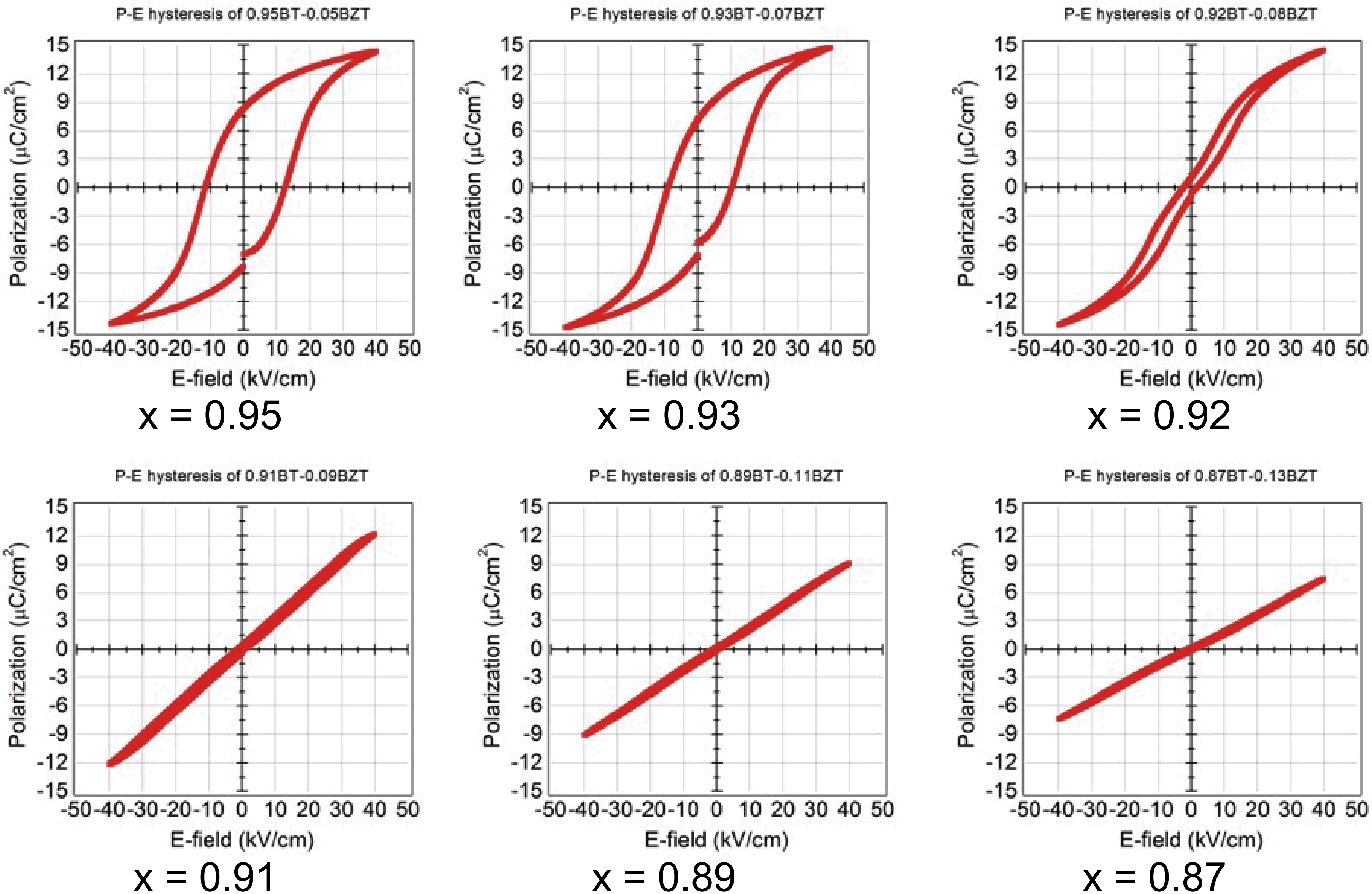








$xBaTiO_3 – (1\text{-}x)Bi(Zn_{0.5}Ti_{0.5})O_3$



$xBaTiO_3 – (1-x)Bi(Zn_{0.5}Ti_{0.5})O_3$

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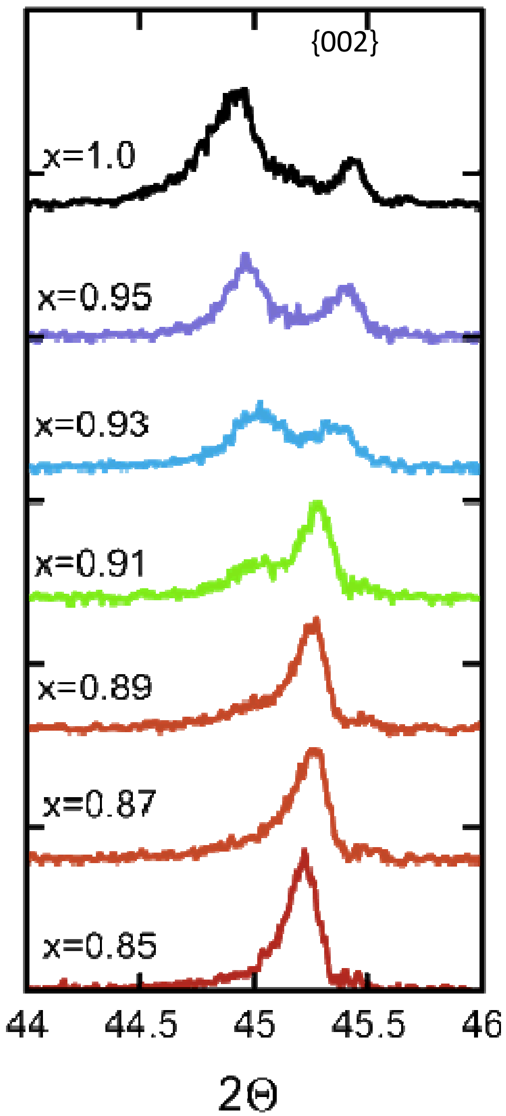
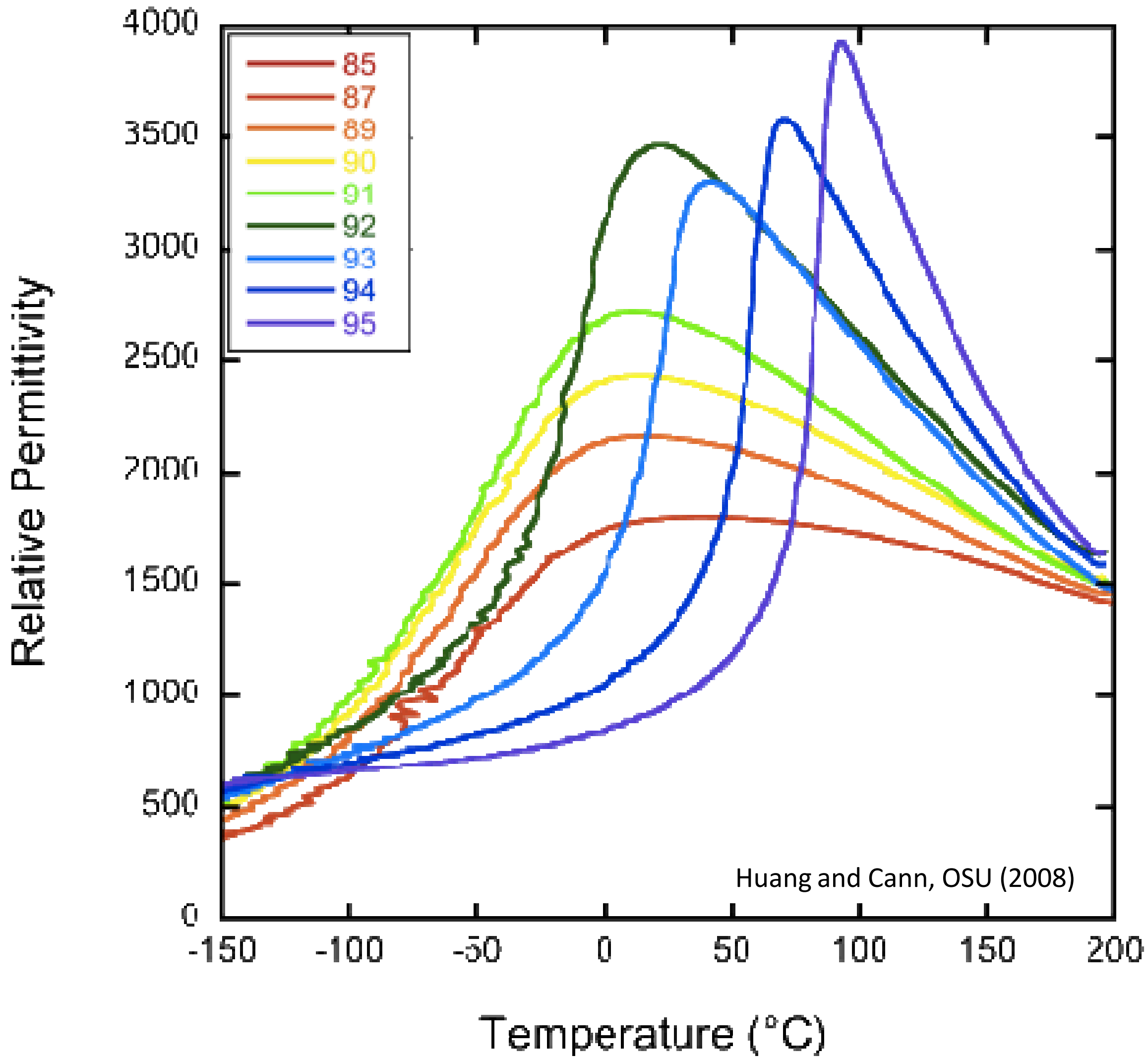
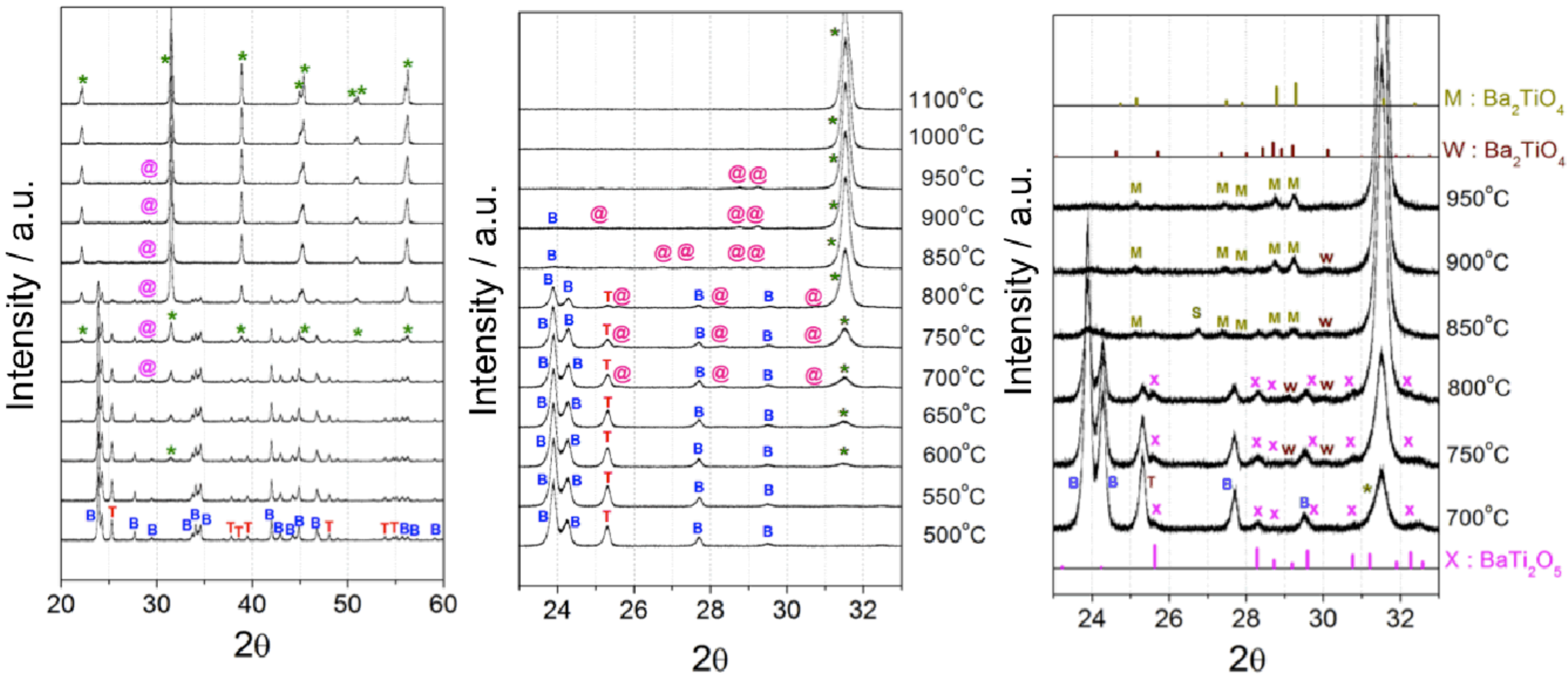


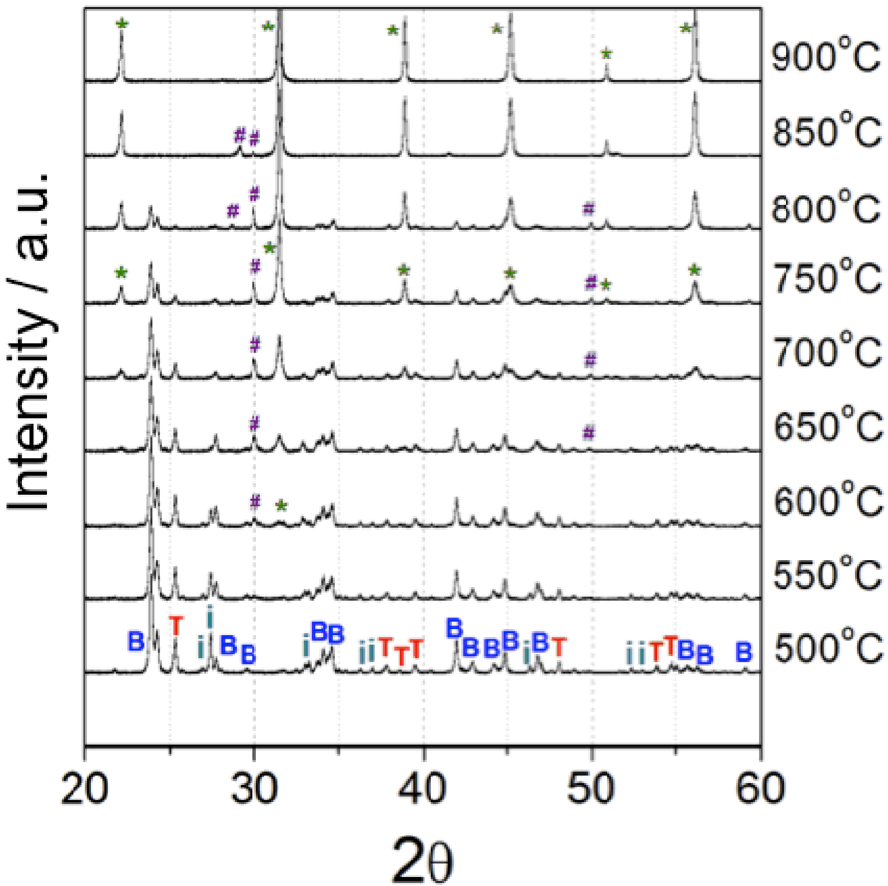


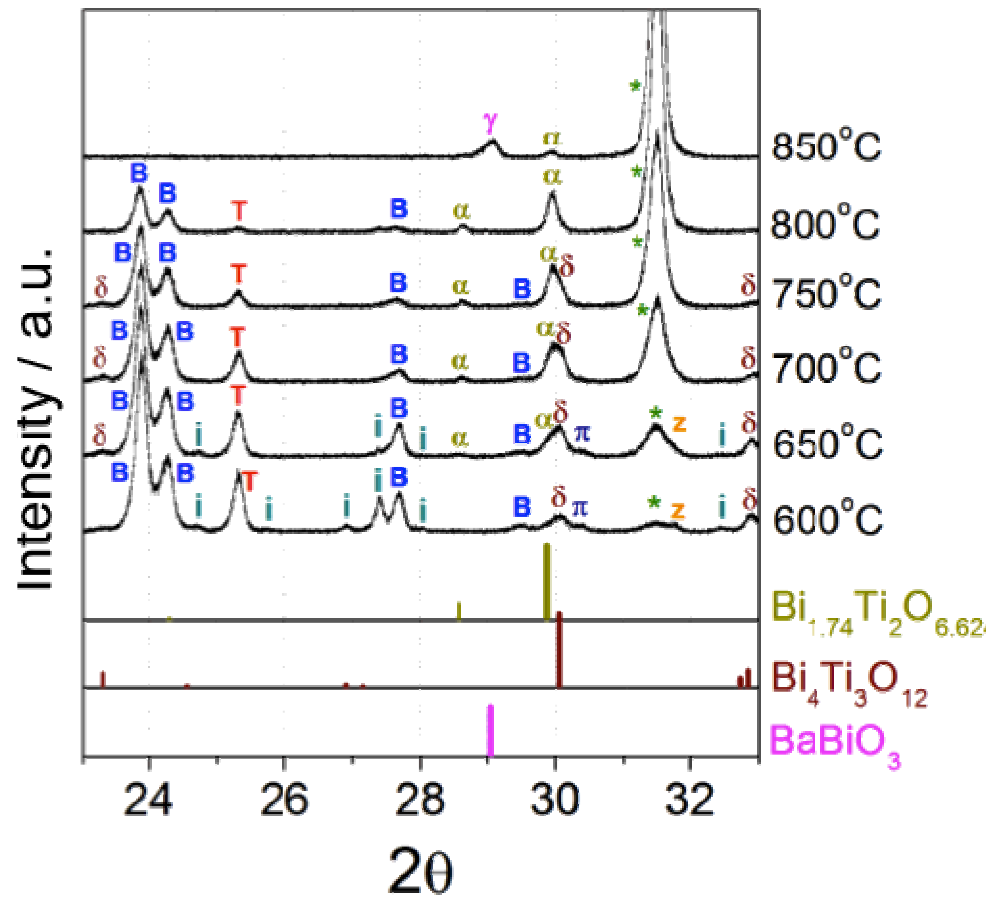
Calcination: $BaTiO_3$



Phase evolution is limited by reaction of $BaCO_3$, proceeds via $BaTi_2O_5$ and Ba_2TiO_4 phases

Calcination: $BaTiO_3$ - $Bi(Zn_{0.5}Ti_{0.5})O_3$

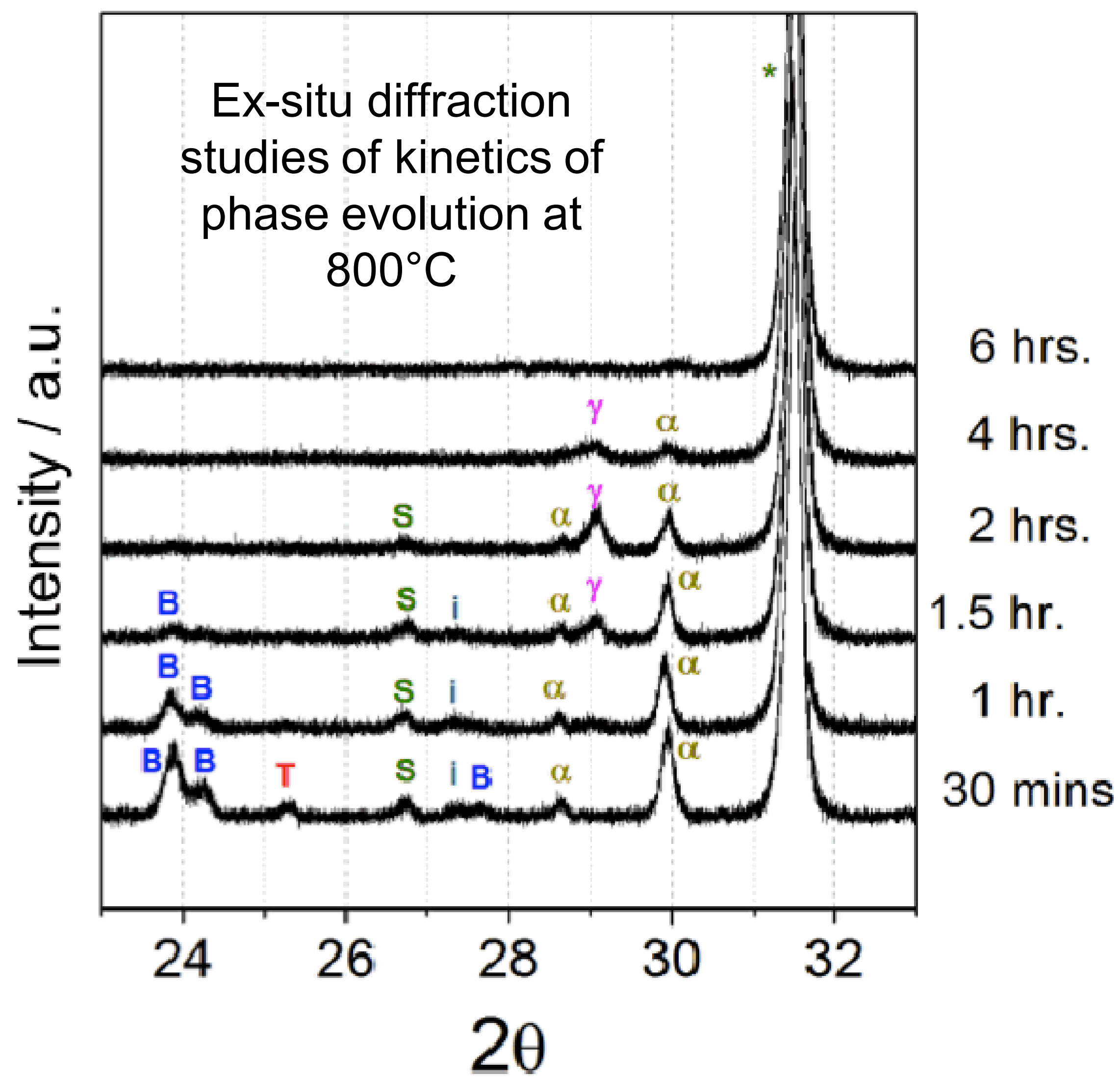




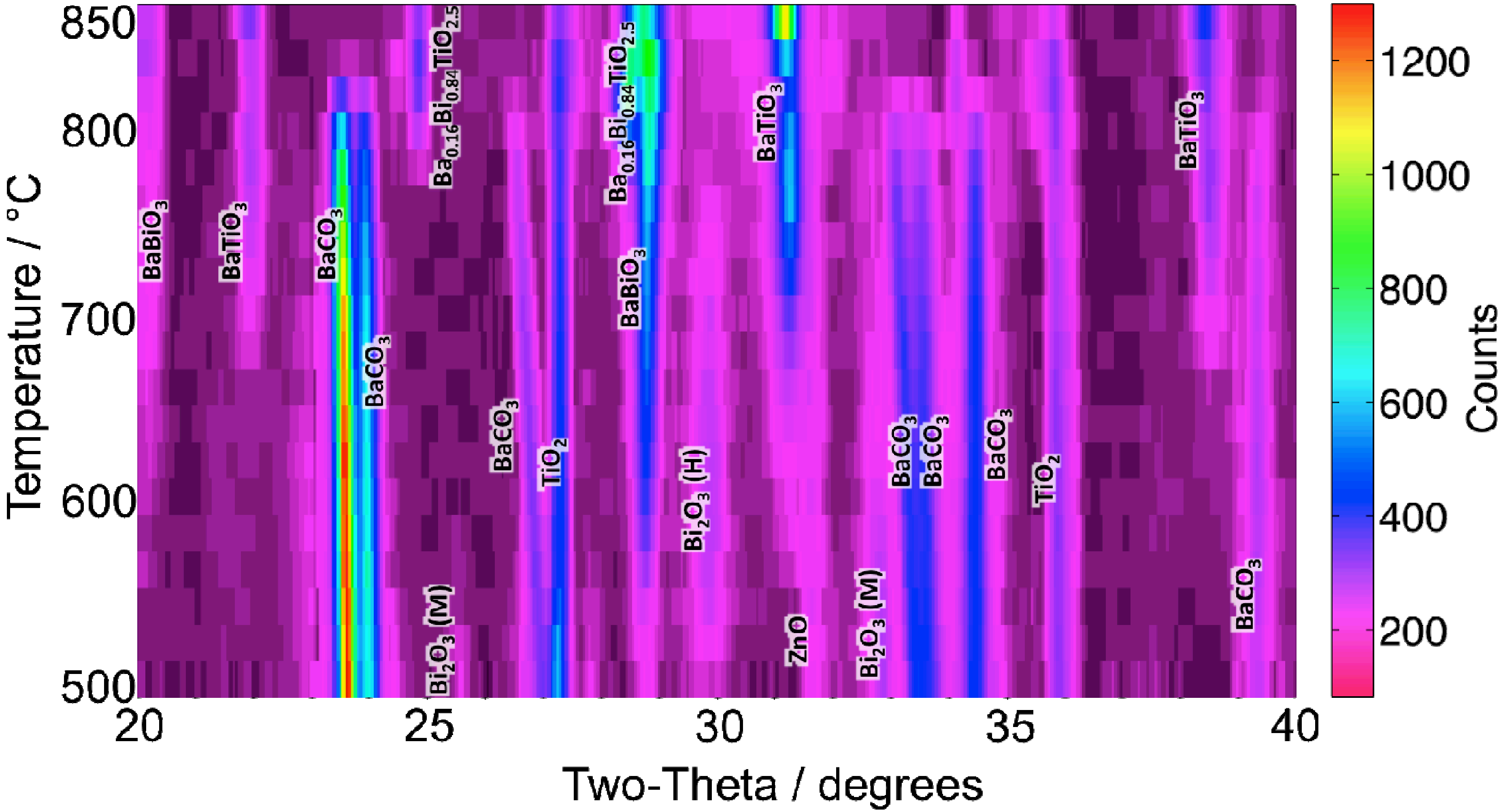
Complex phase evolution with at least 3 intermediate phases, but BZT additions result in single-phase perovskite 200°C lower than pure $BaTiO_3$

Calcination: $BaTiO_3$ - $Bi(Zn_{0.5}Ti_{0.5})O_3$

Phase development via mixed-Bi-valence $BaBiO_3$ phase (likely with significant substitution on both sites…) appears to be critically important for microstructure development.

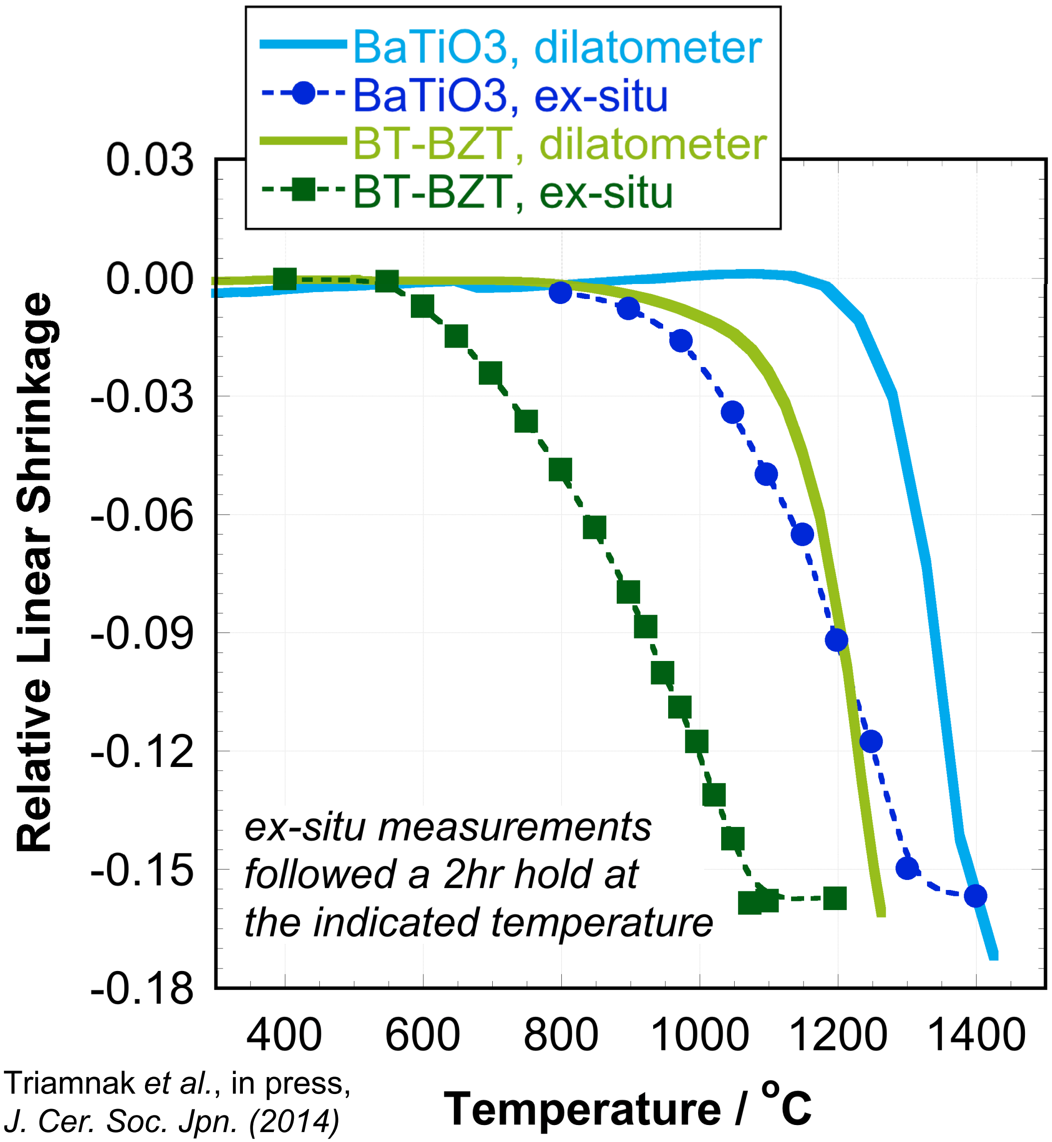


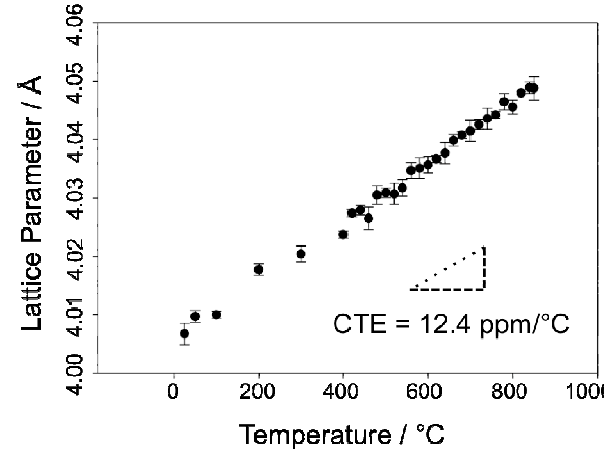
Calcination

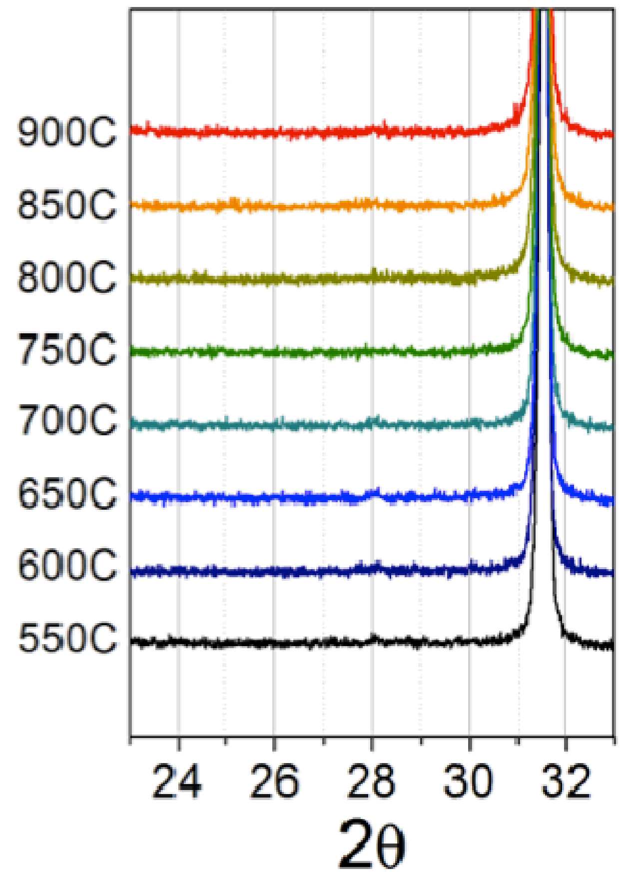


Triamnak *et al.*, in press,
J. Cer. Soc. Jpn. (2014)

Sintering







Triamnak *et al.*, in press, *J. Cer. Soc. Jpn. (2014)*

Thermally Etched Surface

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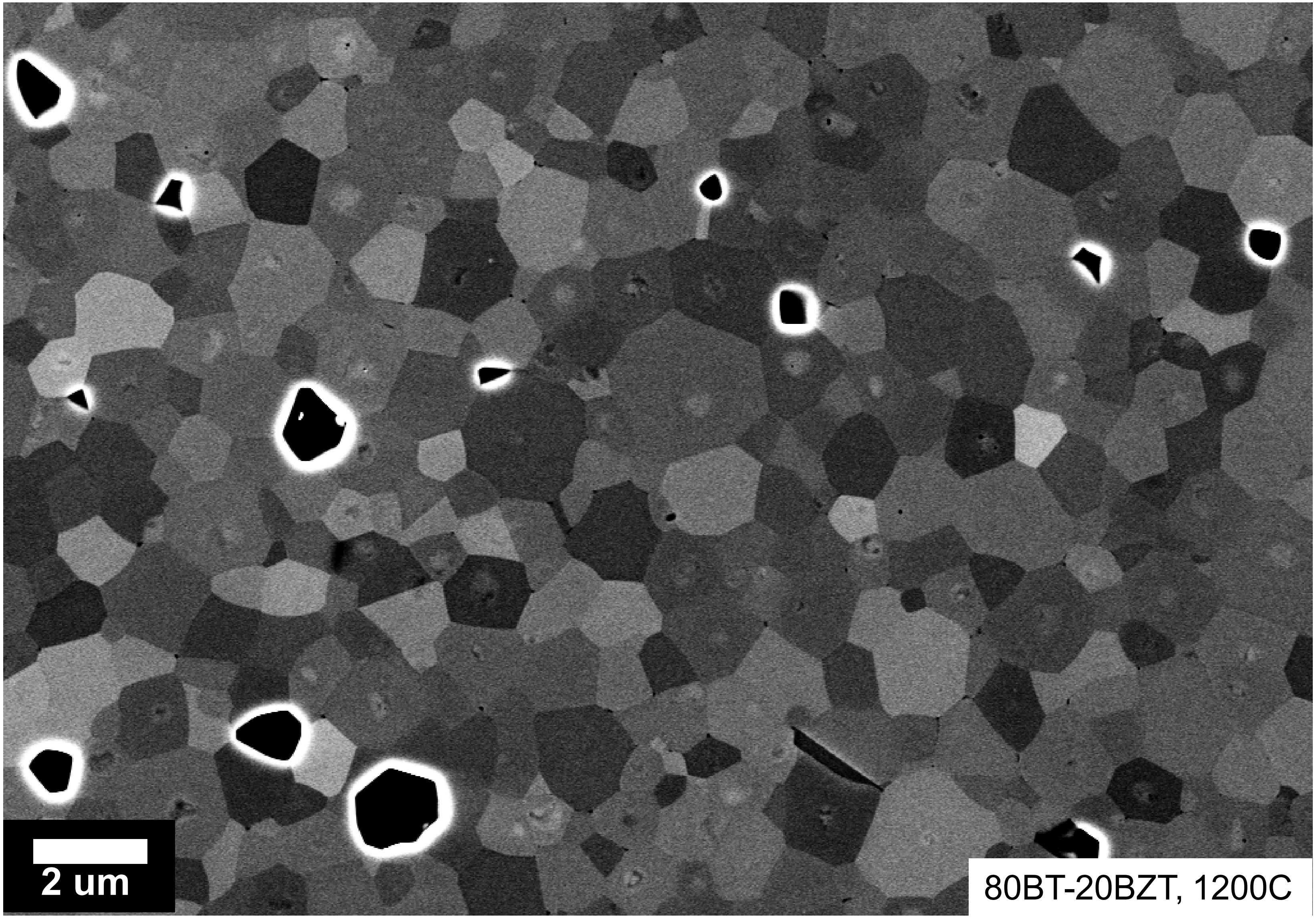
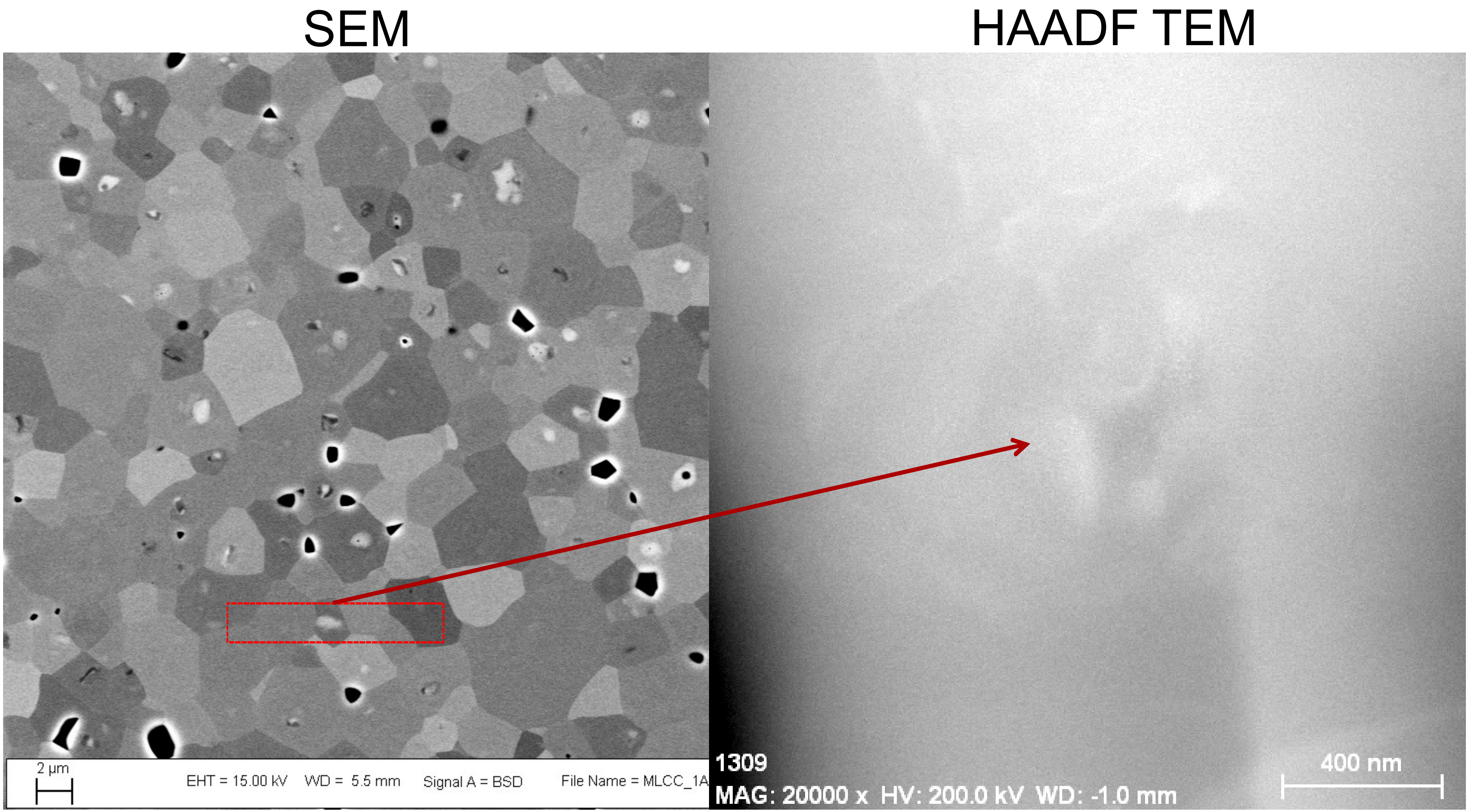
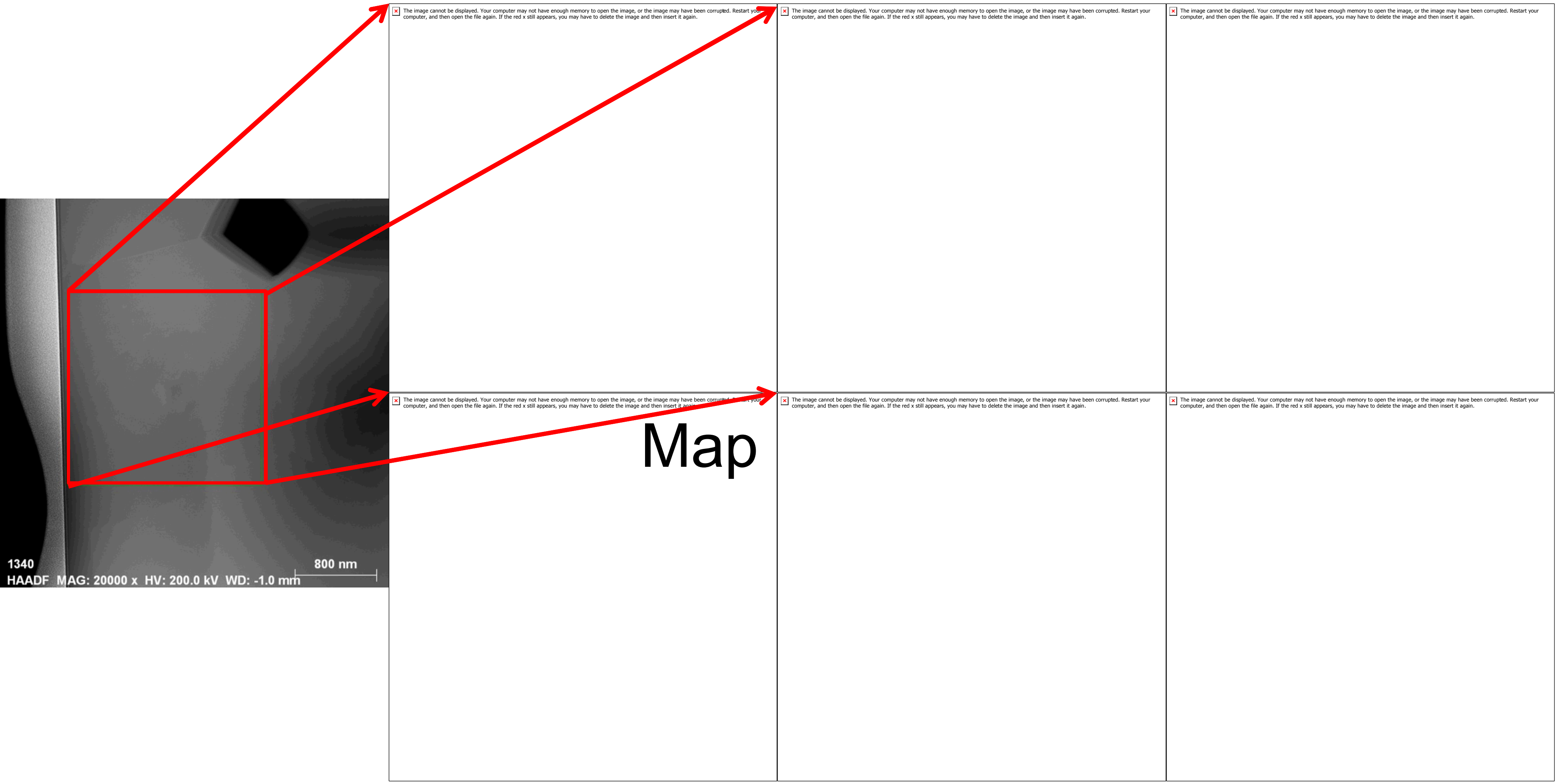
Well-Polished Section, Channeling



Compositional Variation



Bi and Zn Co-segregation



Defect Chemistry Studies

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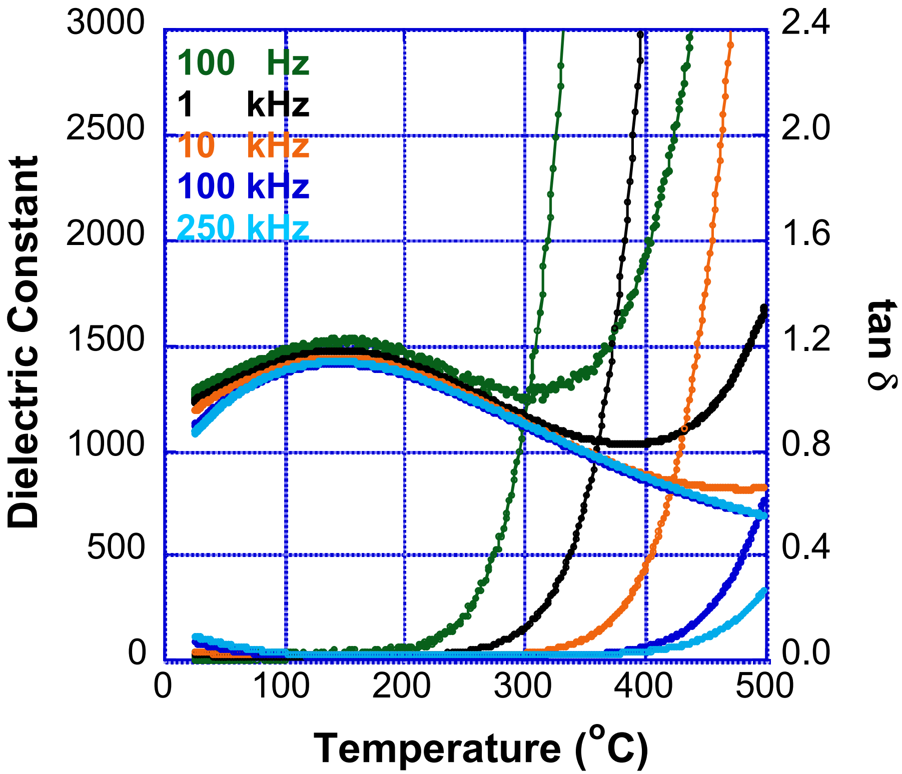
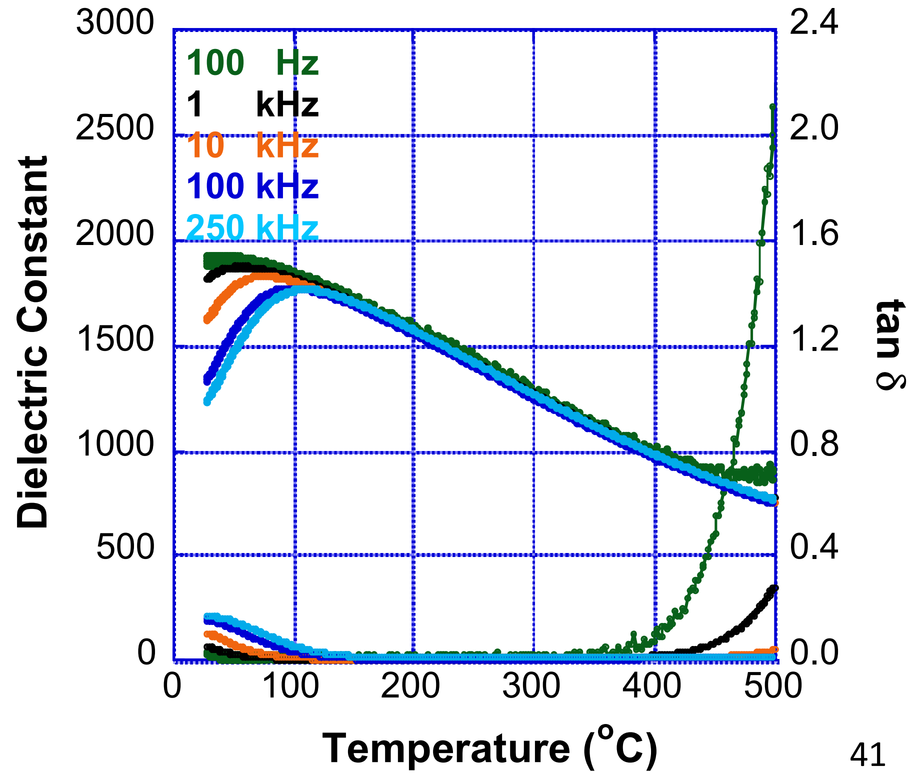
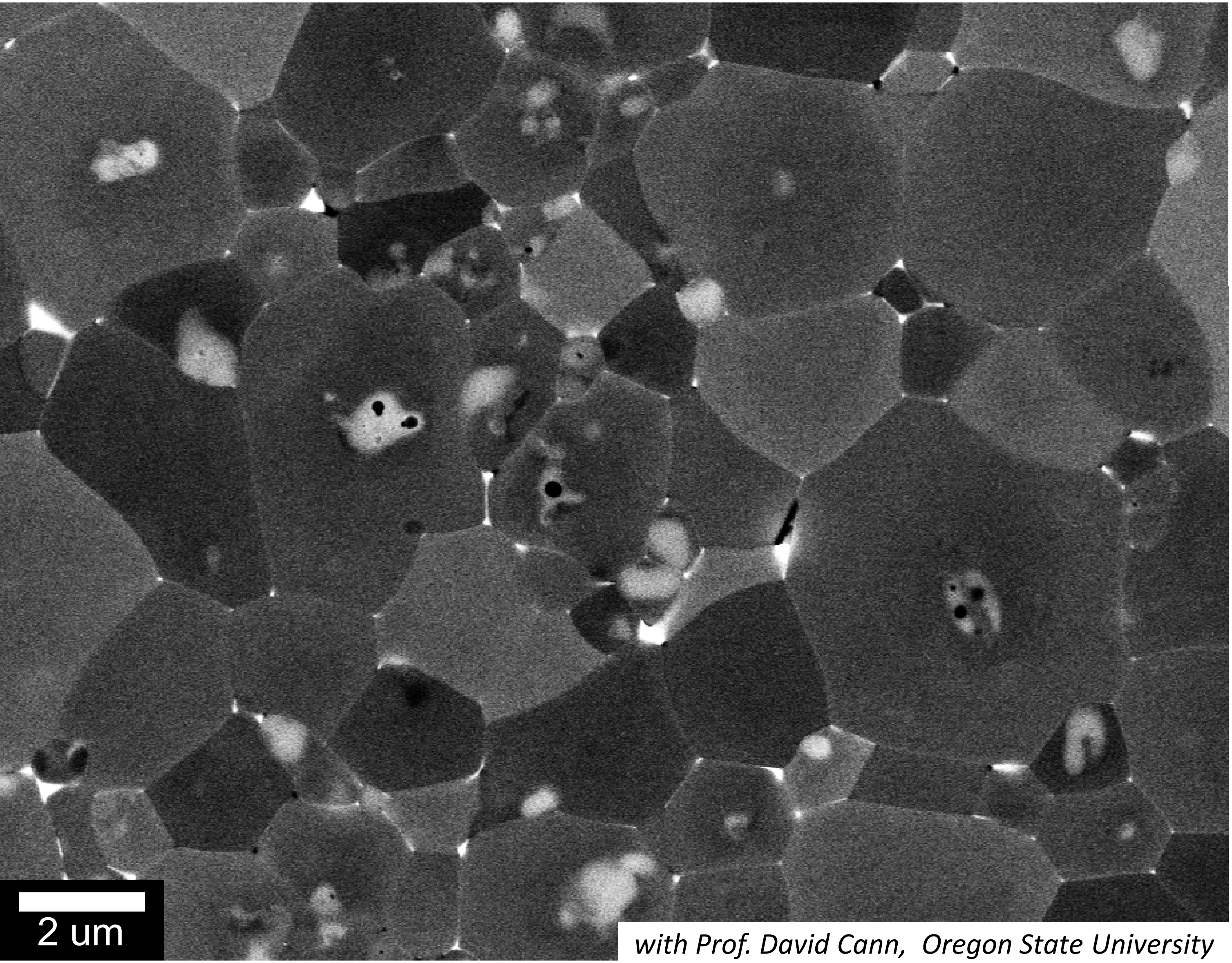
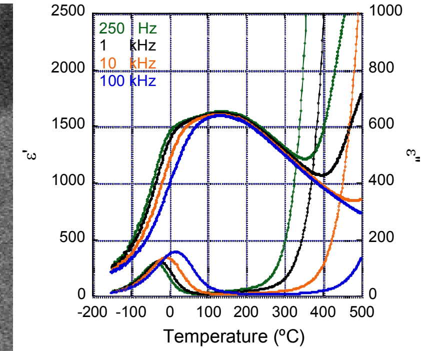
Acceptor	(up to 2mol%) Donor
Low-purity TiO_2 precursor	Ba deficient (compensating)
Ba excess (sub for Bi)	Bi excess (sub for Ba)
Zn excess (sub for Ti)	Ti excess (sub for Zn)
Mn sub for Ti	Nb sub for Ti

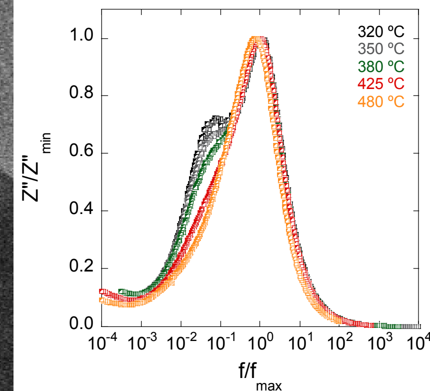


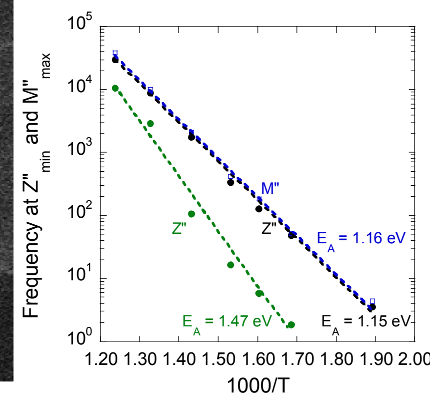


Acceptor Doped









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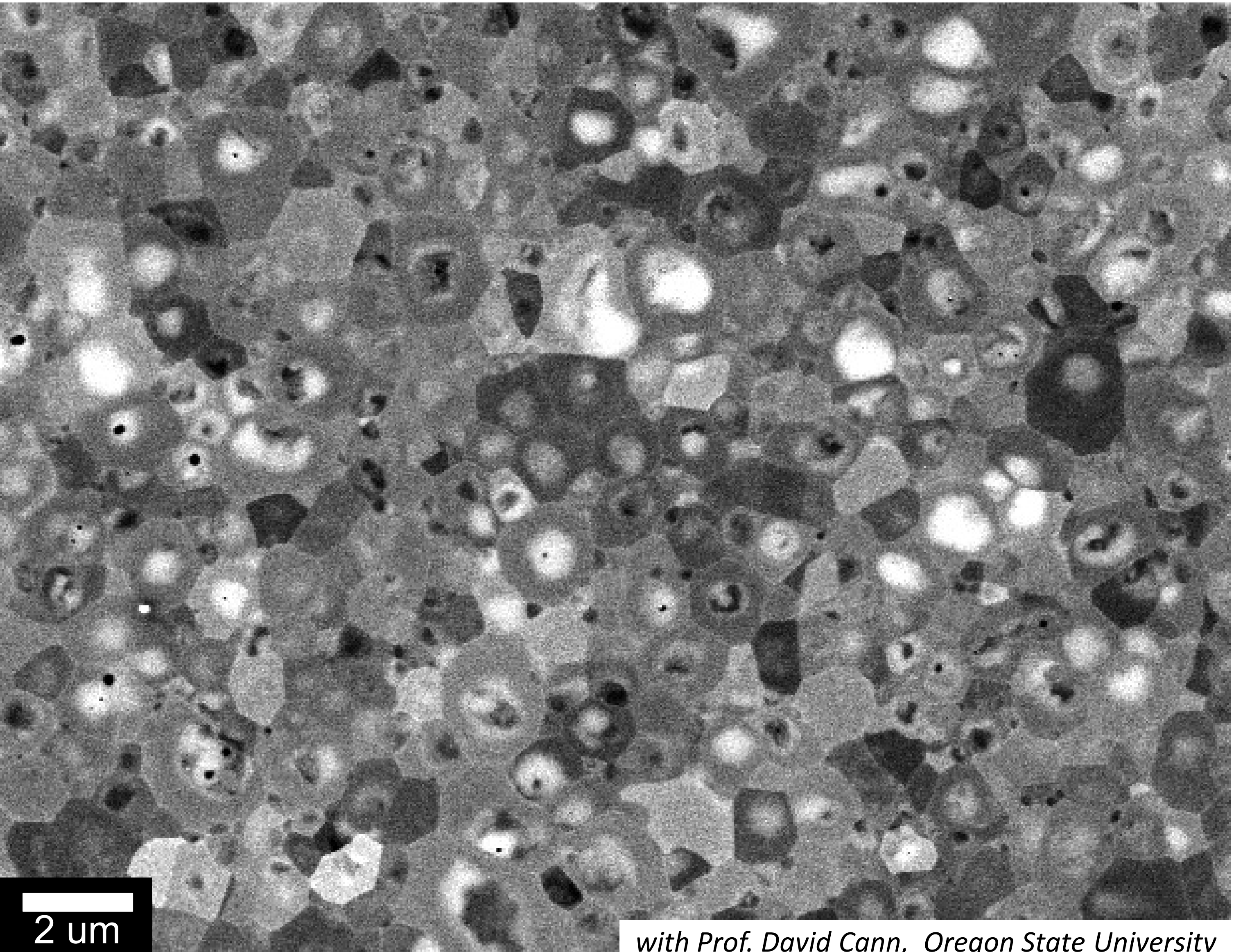
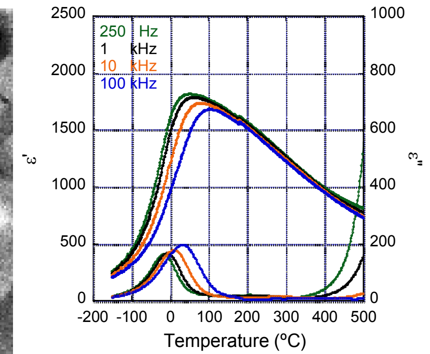
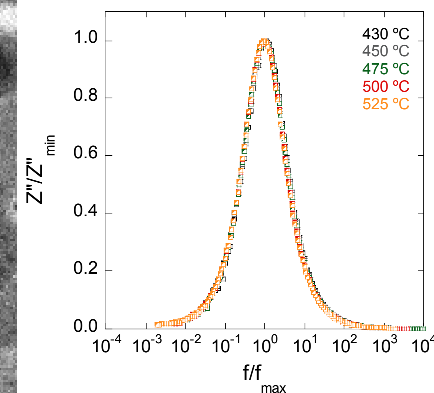
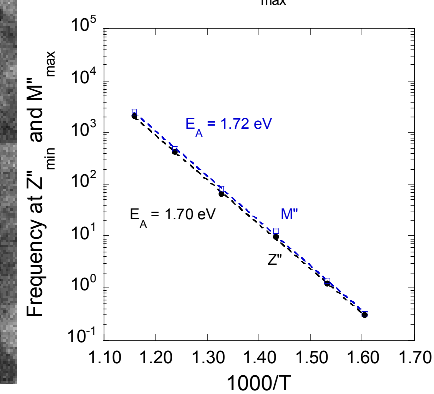
Donor Doped









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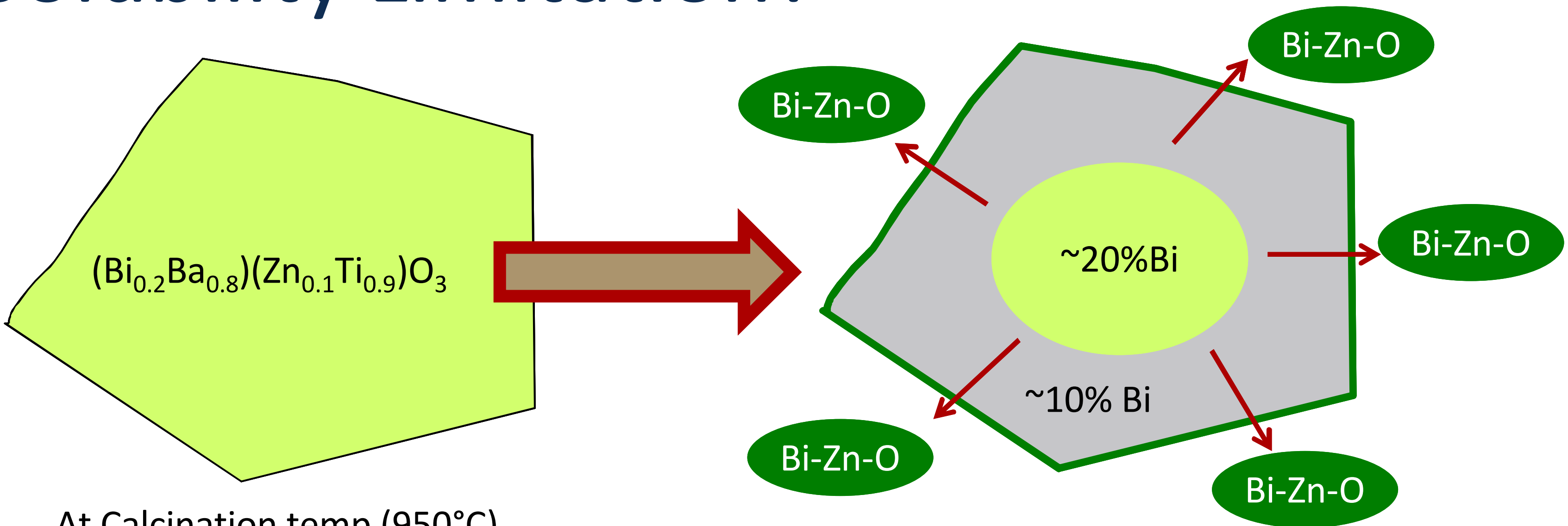
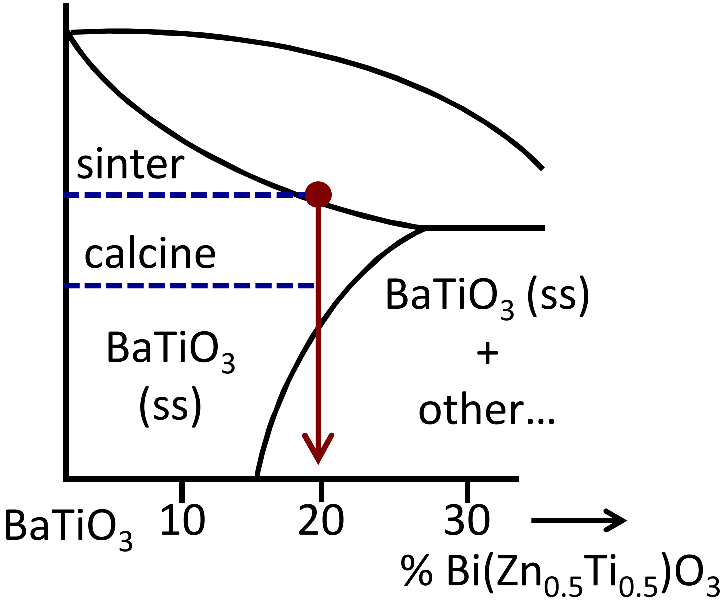
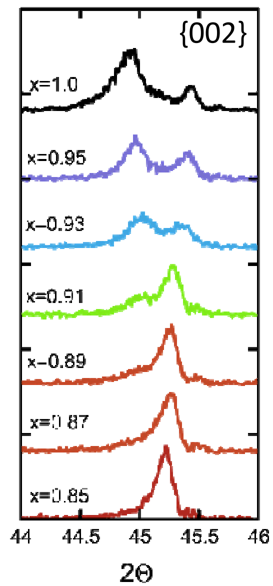
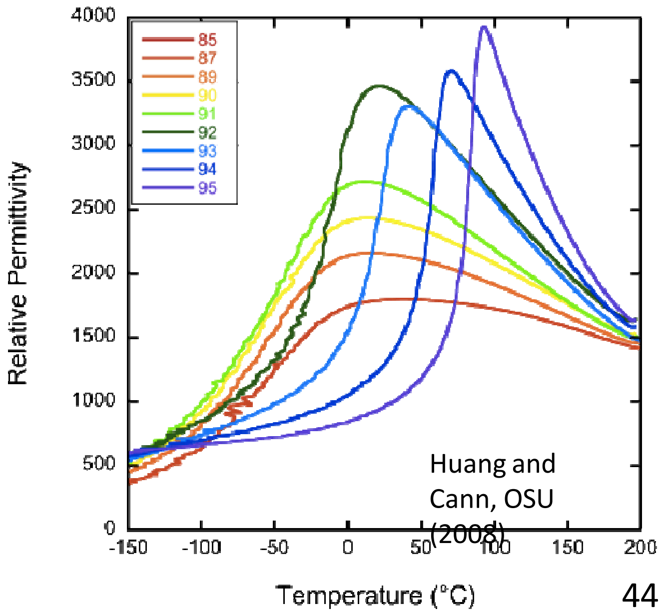
Solubility Limitation?



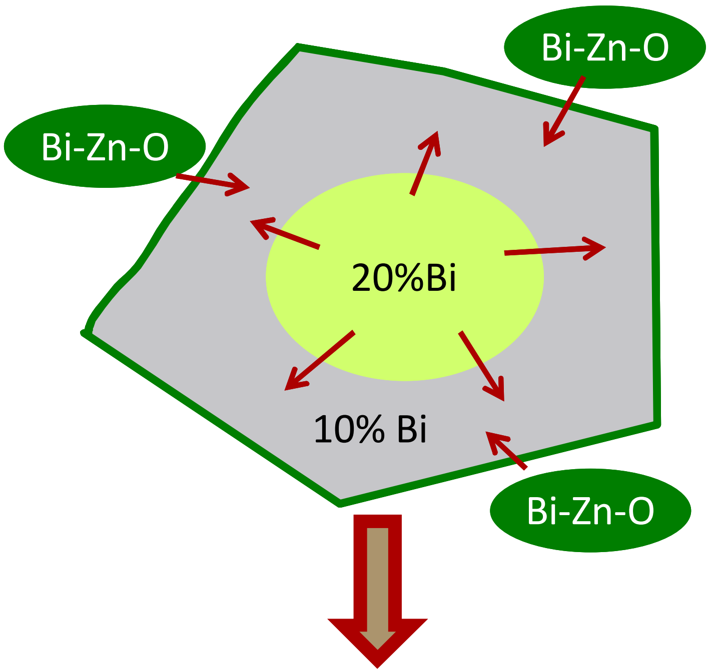
At Calcination temp (950°C)





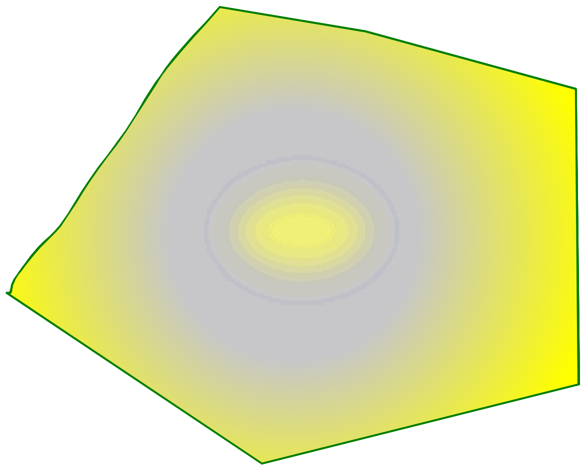


Sintering: Donor doped



Donor Doped: Cation Vacancies Dominate

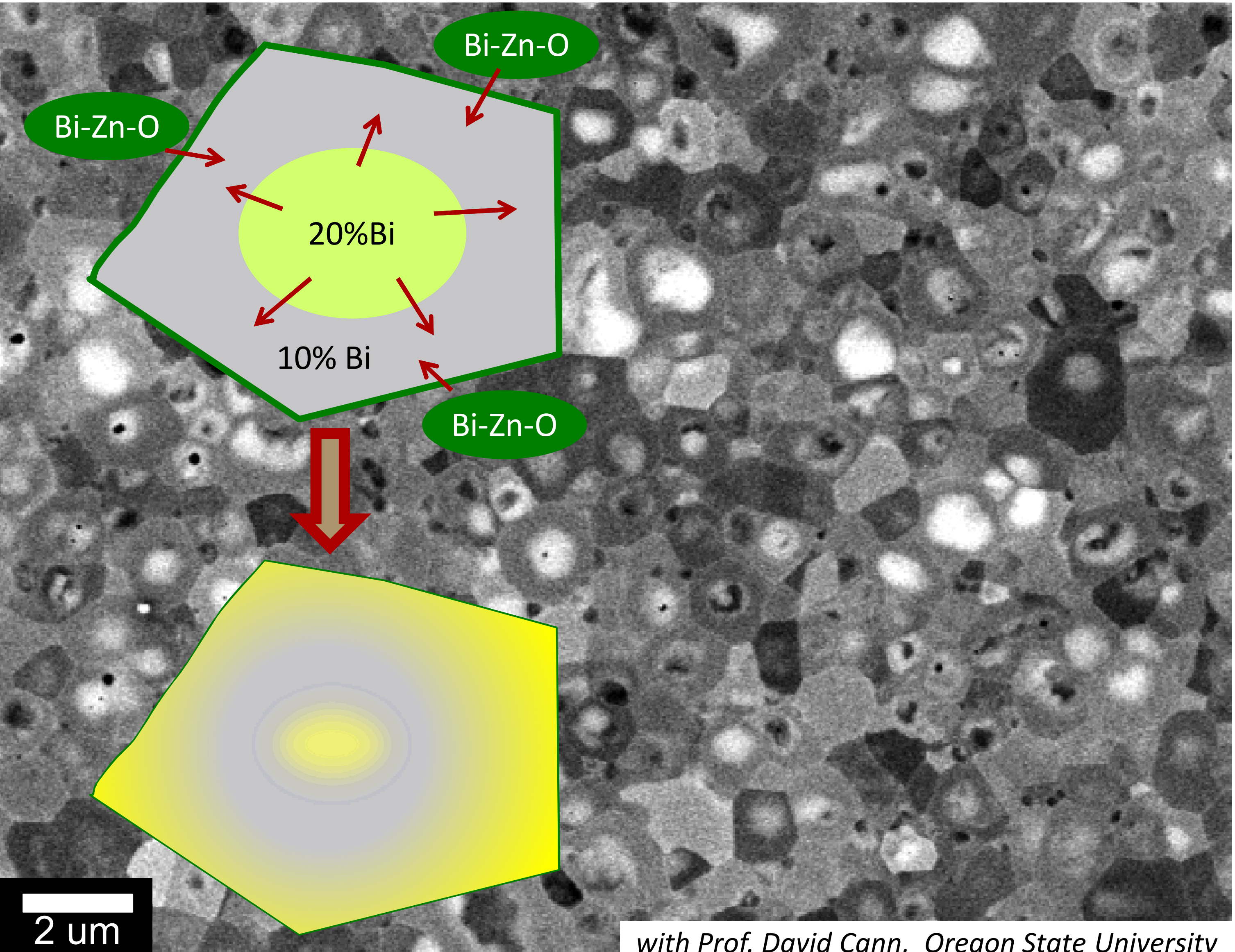
- Bi diffuses in from g.b., out from core
- Diffusion **assisted** by cation vacancies

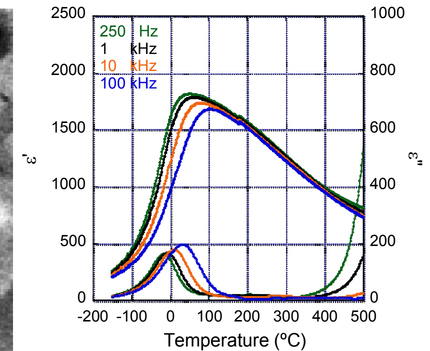


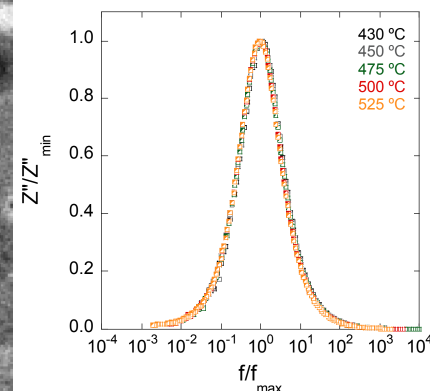
Resultant Microstructure

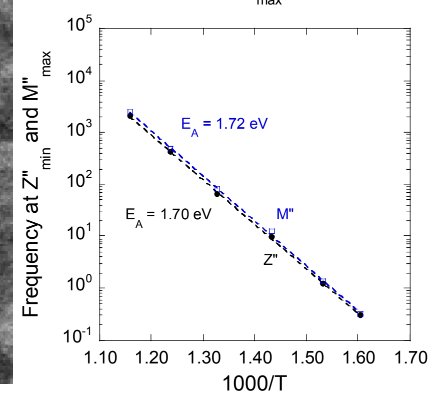
- Relatively homogenous
- Bi-gradient with diffuse boundary due to ample Bi diffusion
- Electrically homogeneous microstructure (single relaxation)

Sintering: Donor doped









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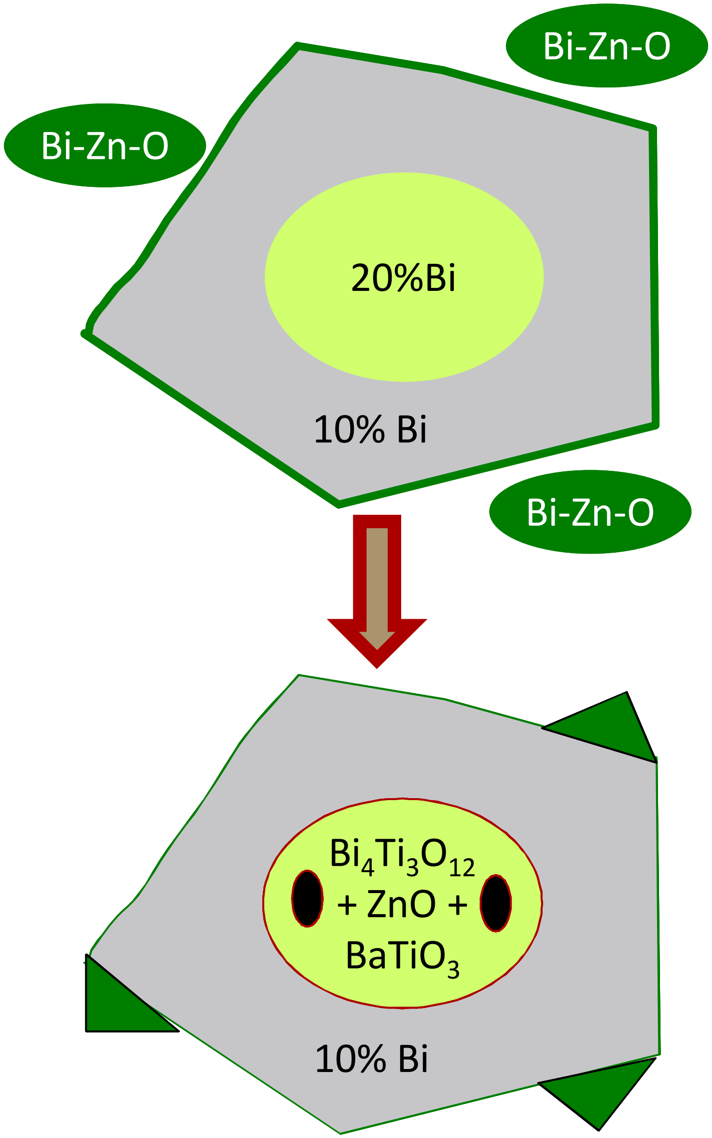
Sintering: Acceptor doped



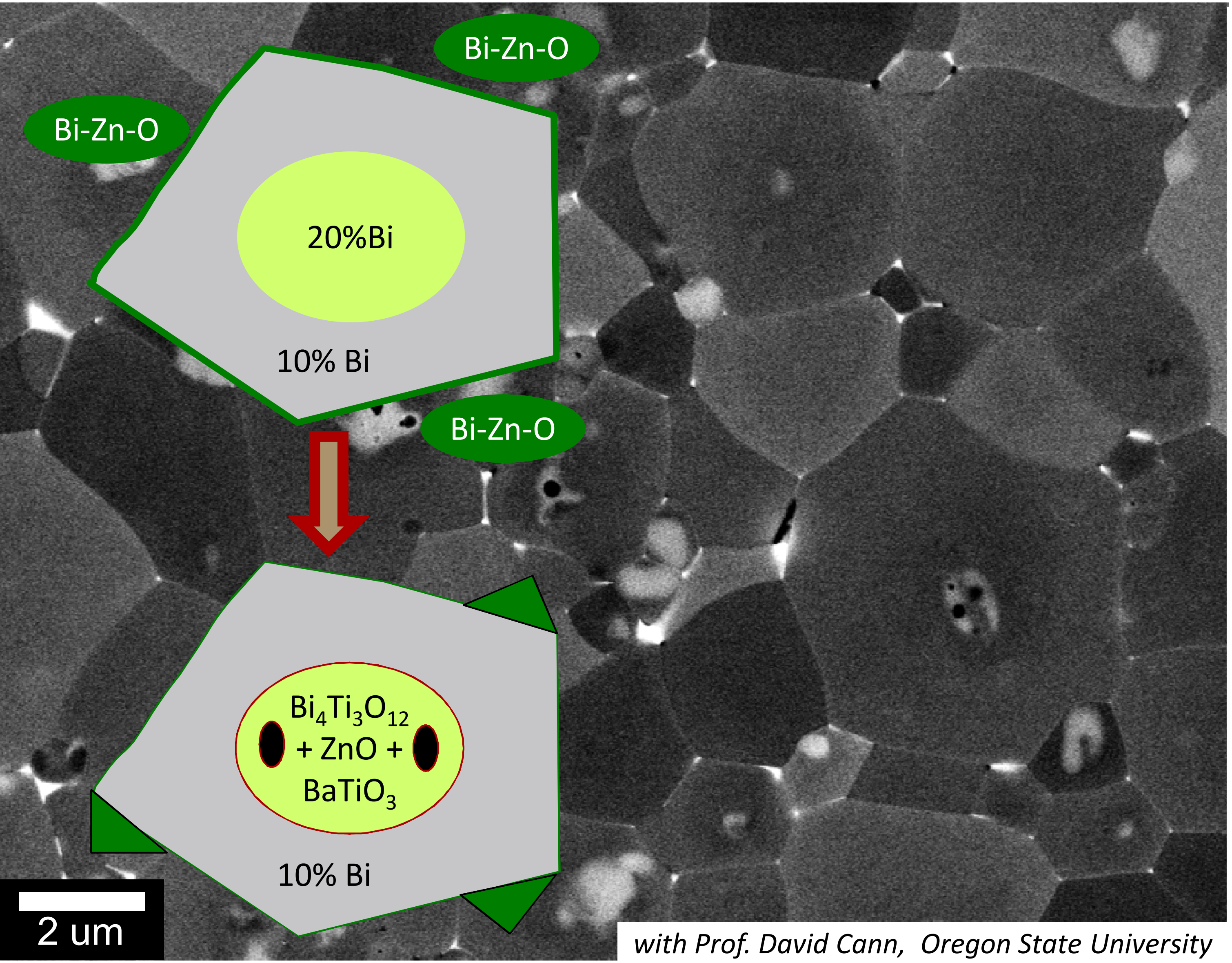
Acceptor Doped: Oxygen Vacancies Dominate

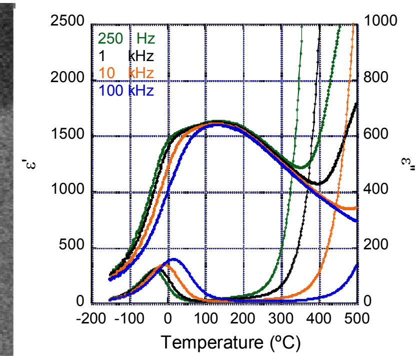
- Bi diffuses in from g.b., out from core
- Diffusion **inhibited** by lack of cation vacancies
- Bi-rich phase at triple points
- Bi-rich cores decompose into equilibrium phases: $Bi_4Ti_3O_{12}$ + ZnO + Ba-Ti-O

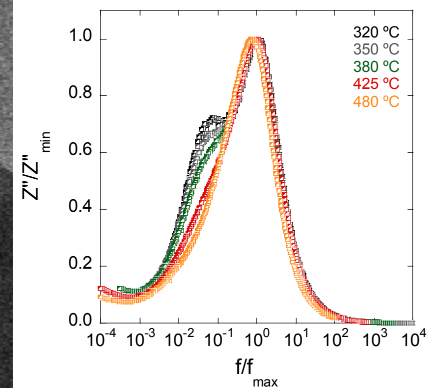
Resultant Microstructure

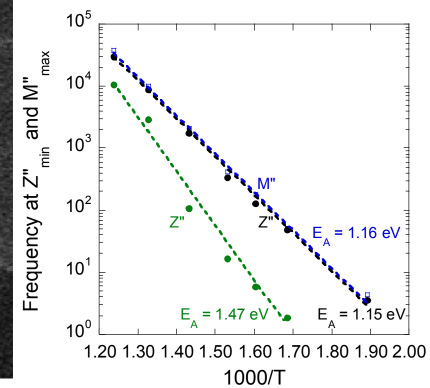
- High-Z phase at triple points
- Well defined core boundary
- Low-Z precipitates in core region
- Electrically heterogeneous microstructure (two relaxations)

Sintering: Acceptor doped









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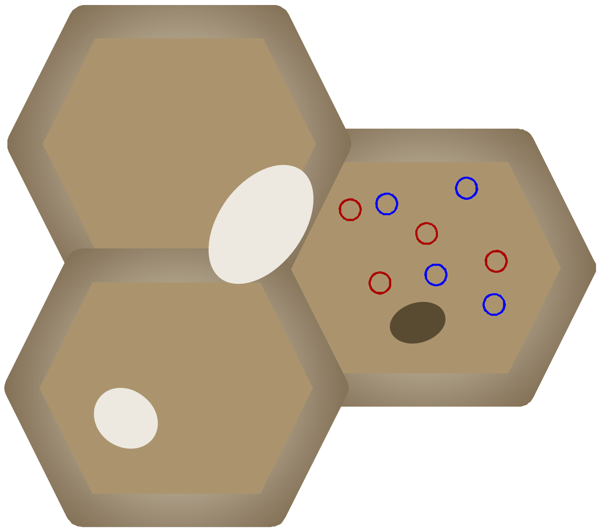
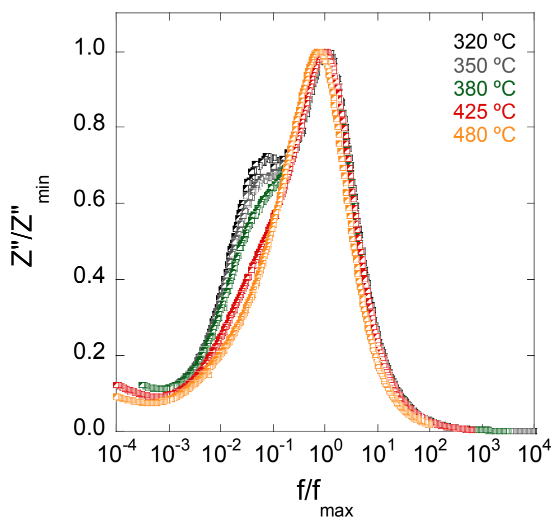
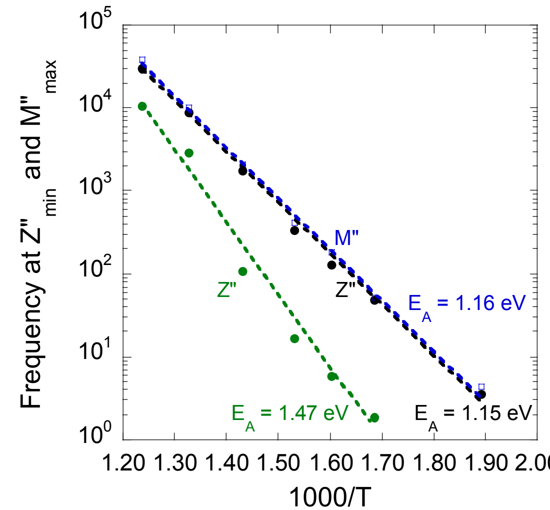
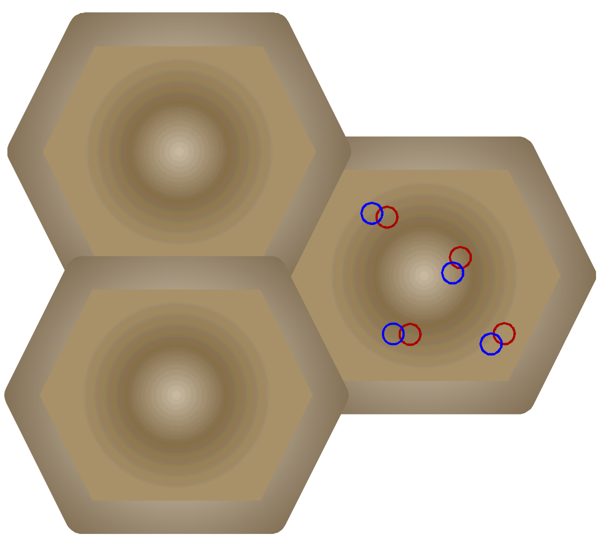
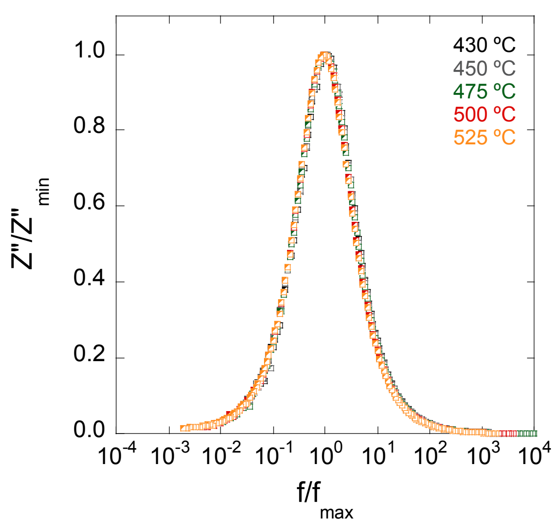
Microscale Heterogeneity

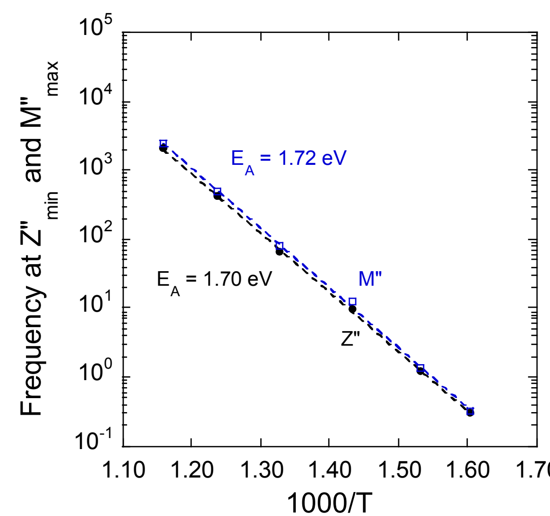












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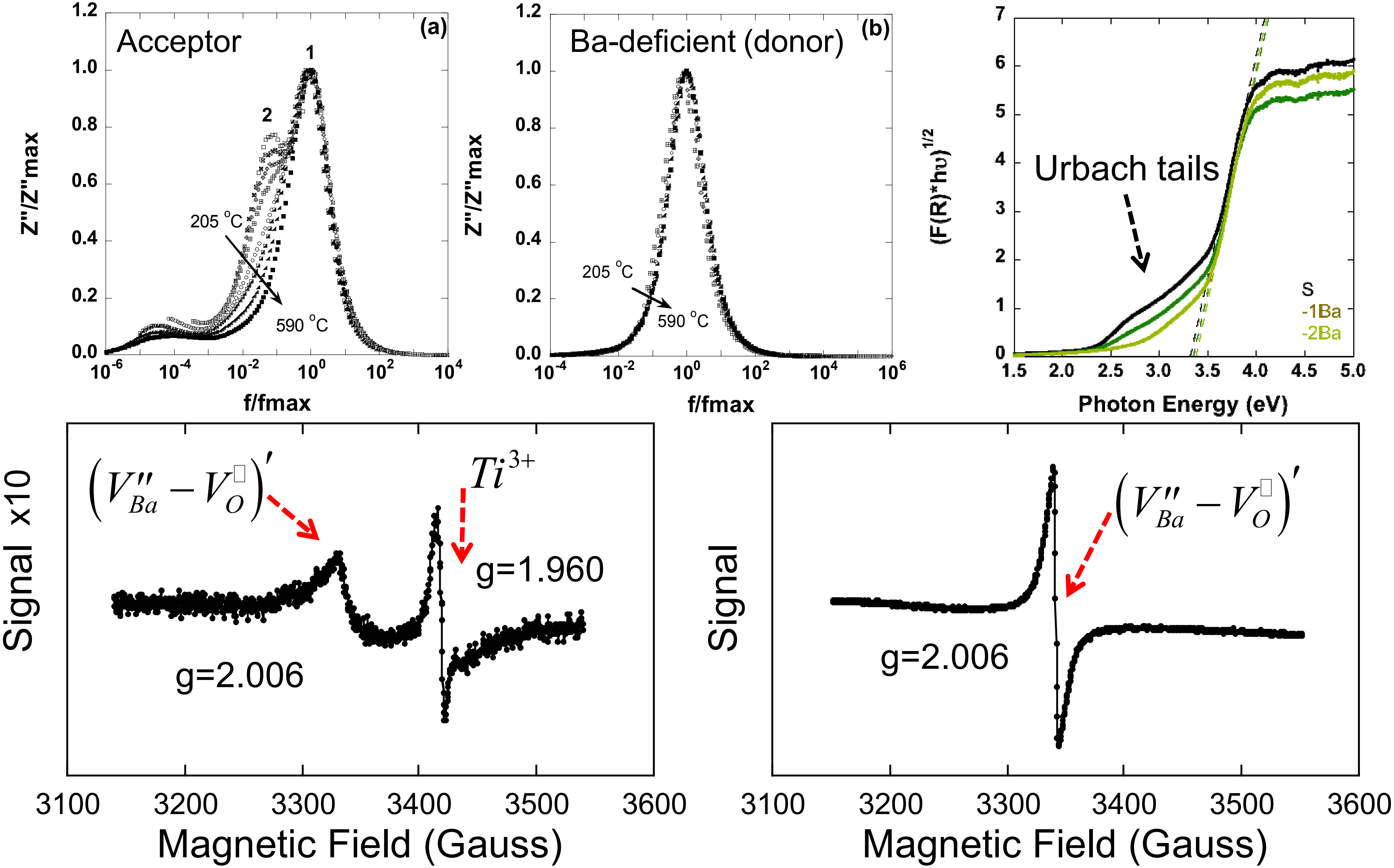
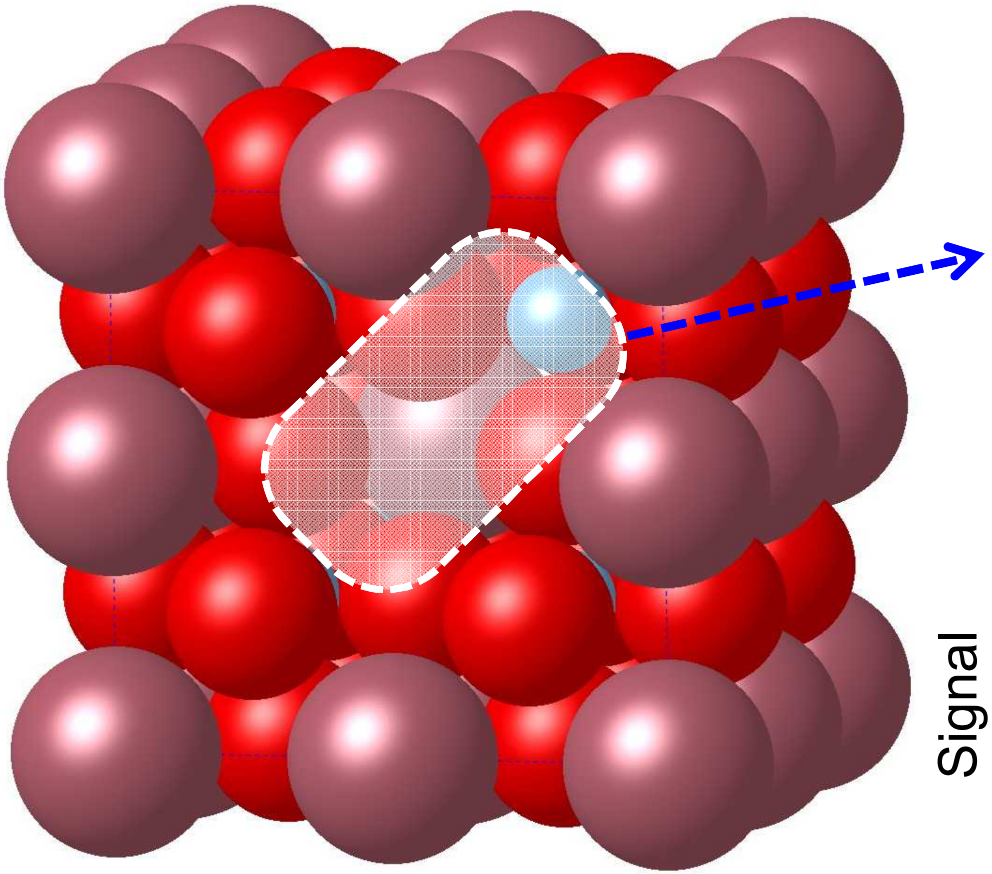
Probing Defects

Raengthon *et al.*, *Appl. Phys. Lett.*, **101** (2012) 112904.

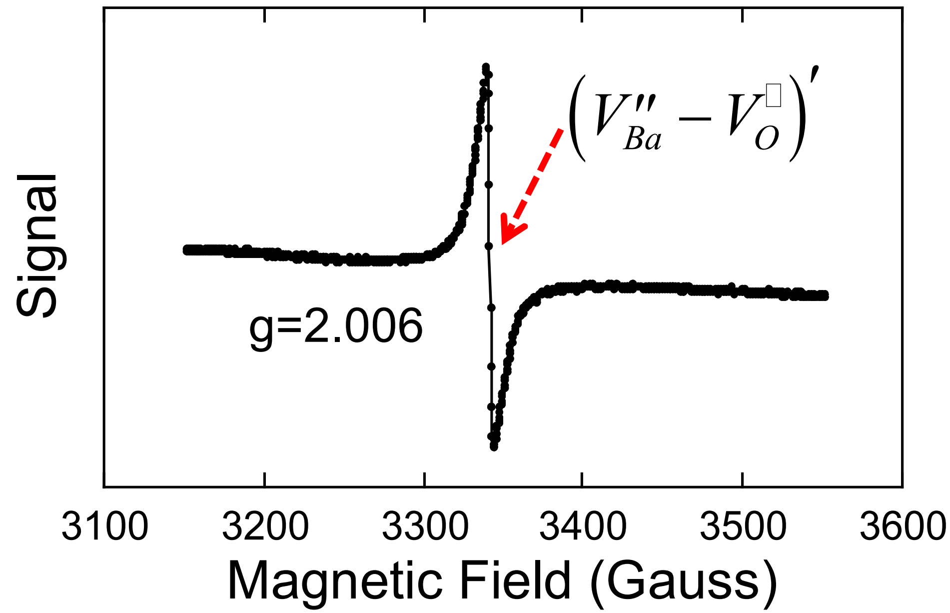


Probing Defects

Raengthon *et al.*, *Appl. Phys. Lett.*, **101** (2012) 112904.

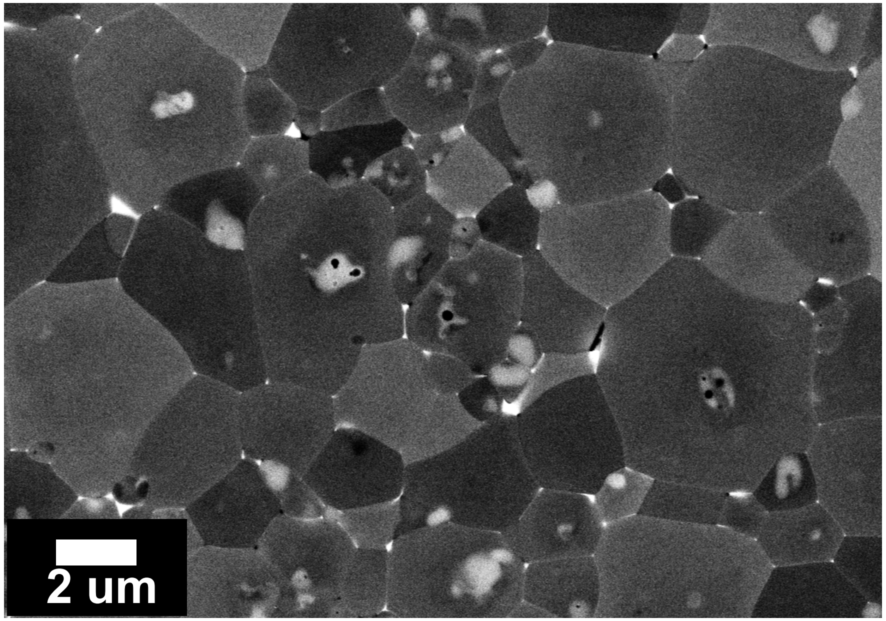


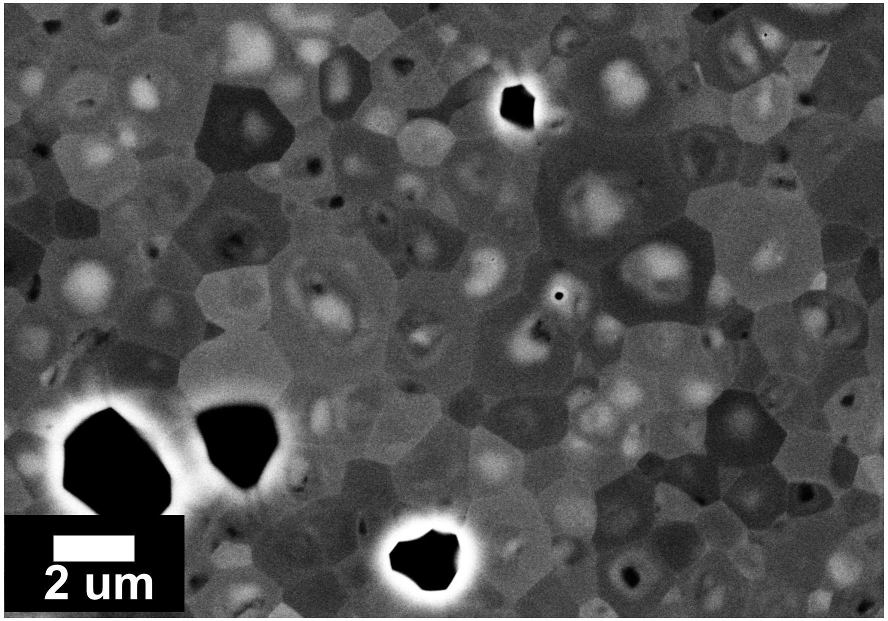
$$\left(V_{Ba}'' - V_O^{\bullet\bullet}\right)$$



Summary

- Complex phase evolution and potential liquid phase(s) enable reduced temperature processing
- Electrical response(s) of weakly-coupled relaxor systems tied to multi-scale chemical heterogeneities
- Tightly bound defects enable high resistivity





Extra Slides Follow