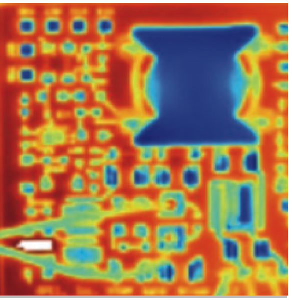
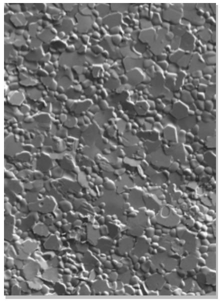
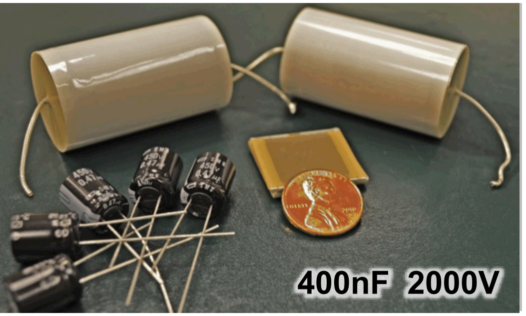
SAND2013-8774C

Ceramic Capacitors based on Temperature and Voltage-Stable Relaxor Dielectrics







Geoff Brennecka, Harlan Brown-Shaklee, John Borchardt, and Mia Blea-Kirby

Sandia National Laboratories

Natthaphon Raengthon and David Cann

Oregon State University

Kevin Ring

New Mexico Tech

Sandia National Laboratories

Exceptional service in the national interest

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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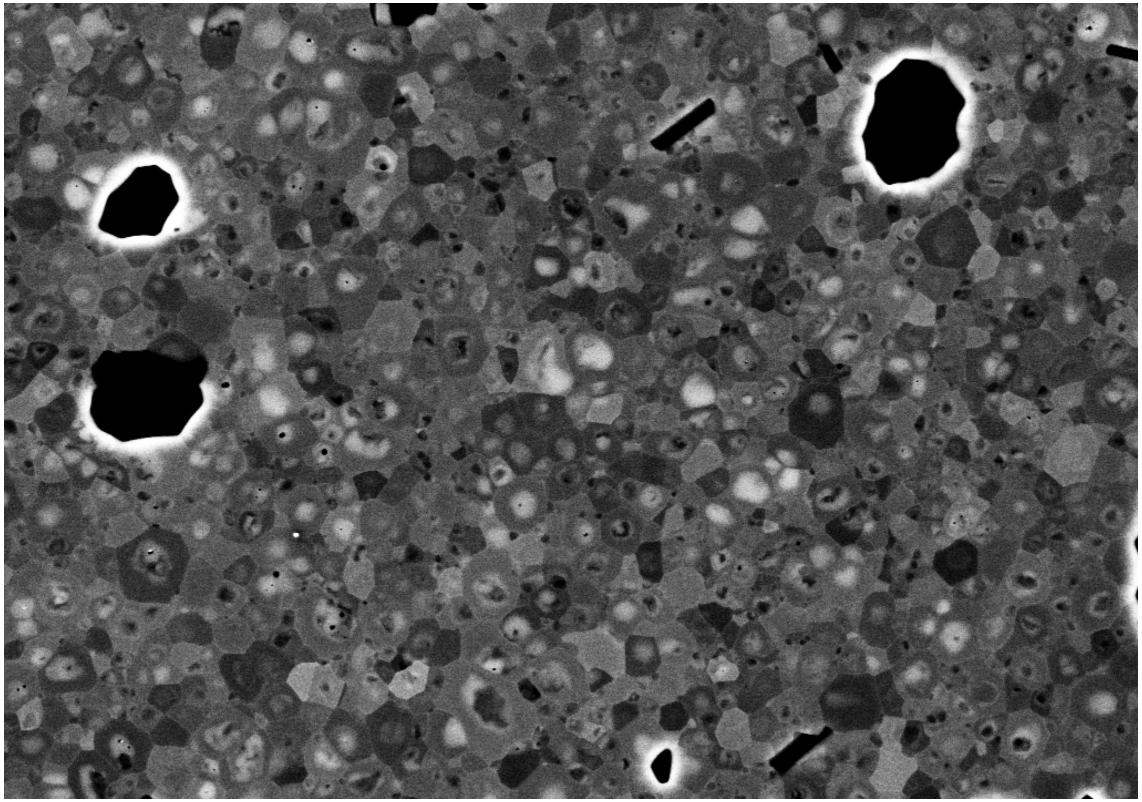
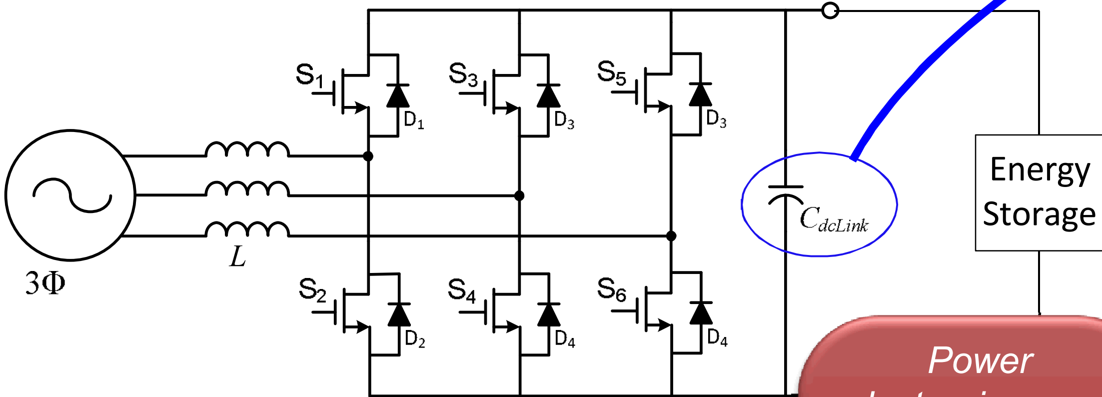
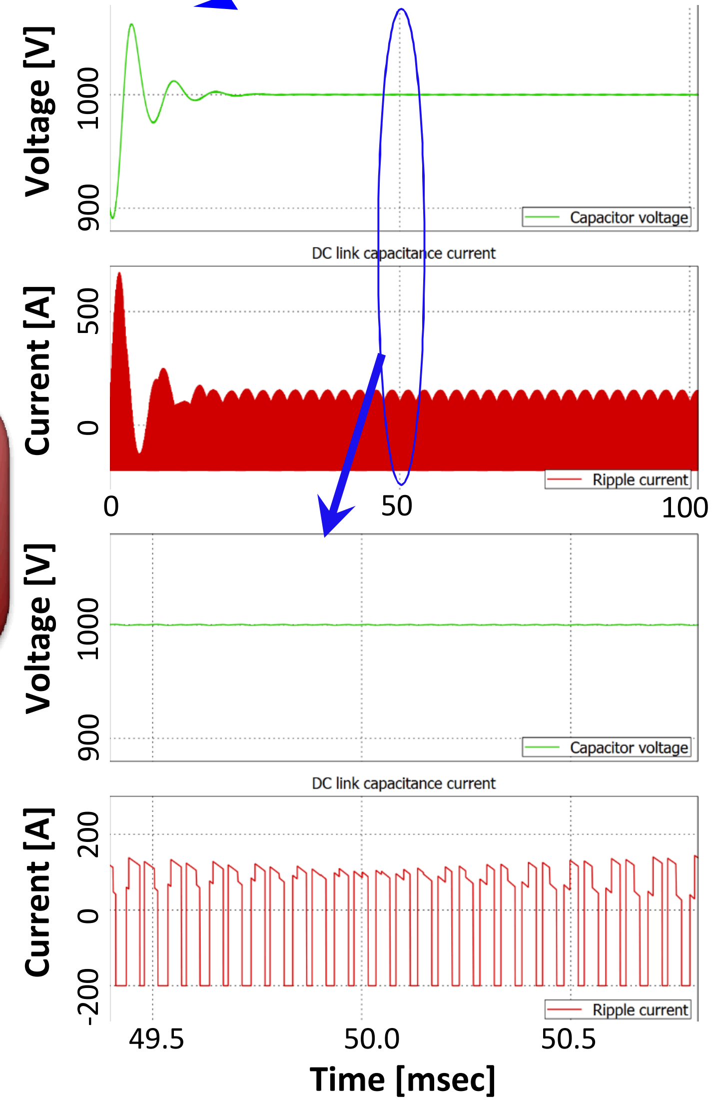


Application Space



Power electronics need high operating temperature, low ESR, high resistivity

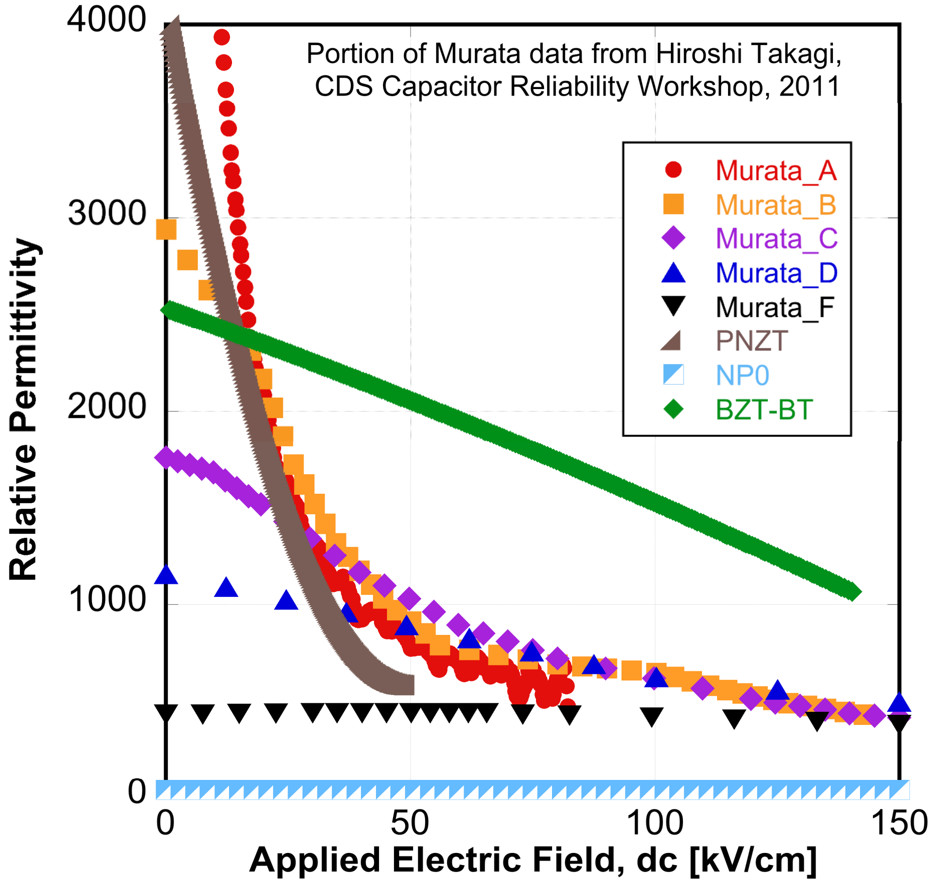


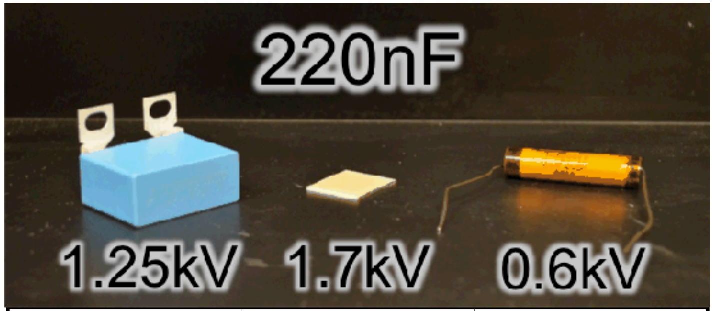
Pulse discharge applications require high energy density, low electromechanical response, low ESR

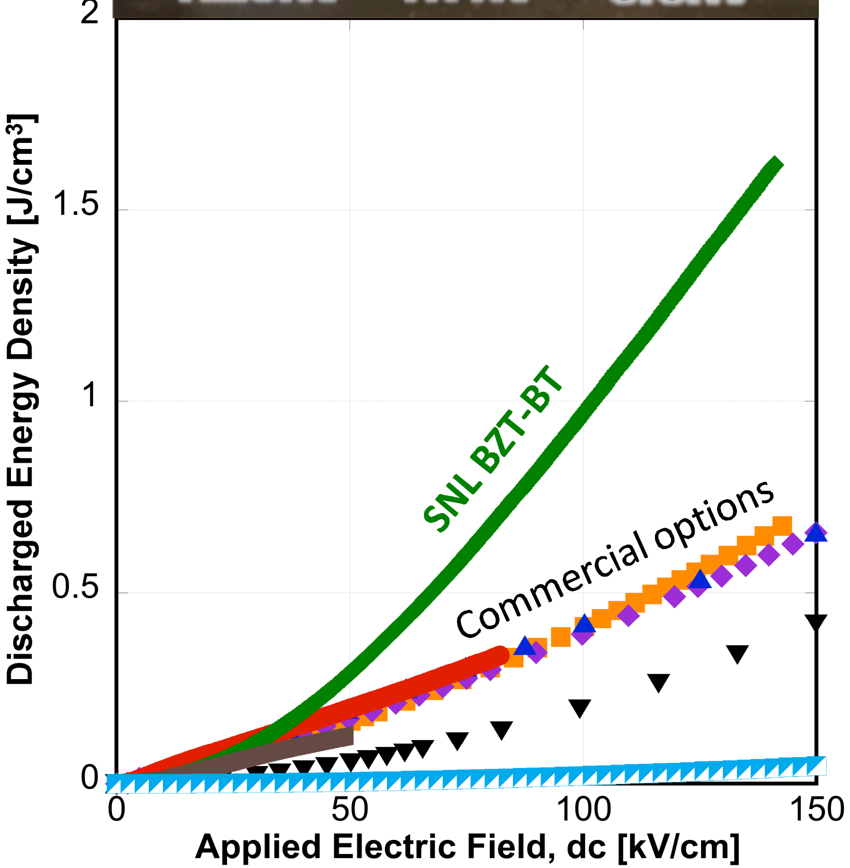
Simulation courtesy of Eric Green and Stan Atcitty

High Energy Density Dielectrics

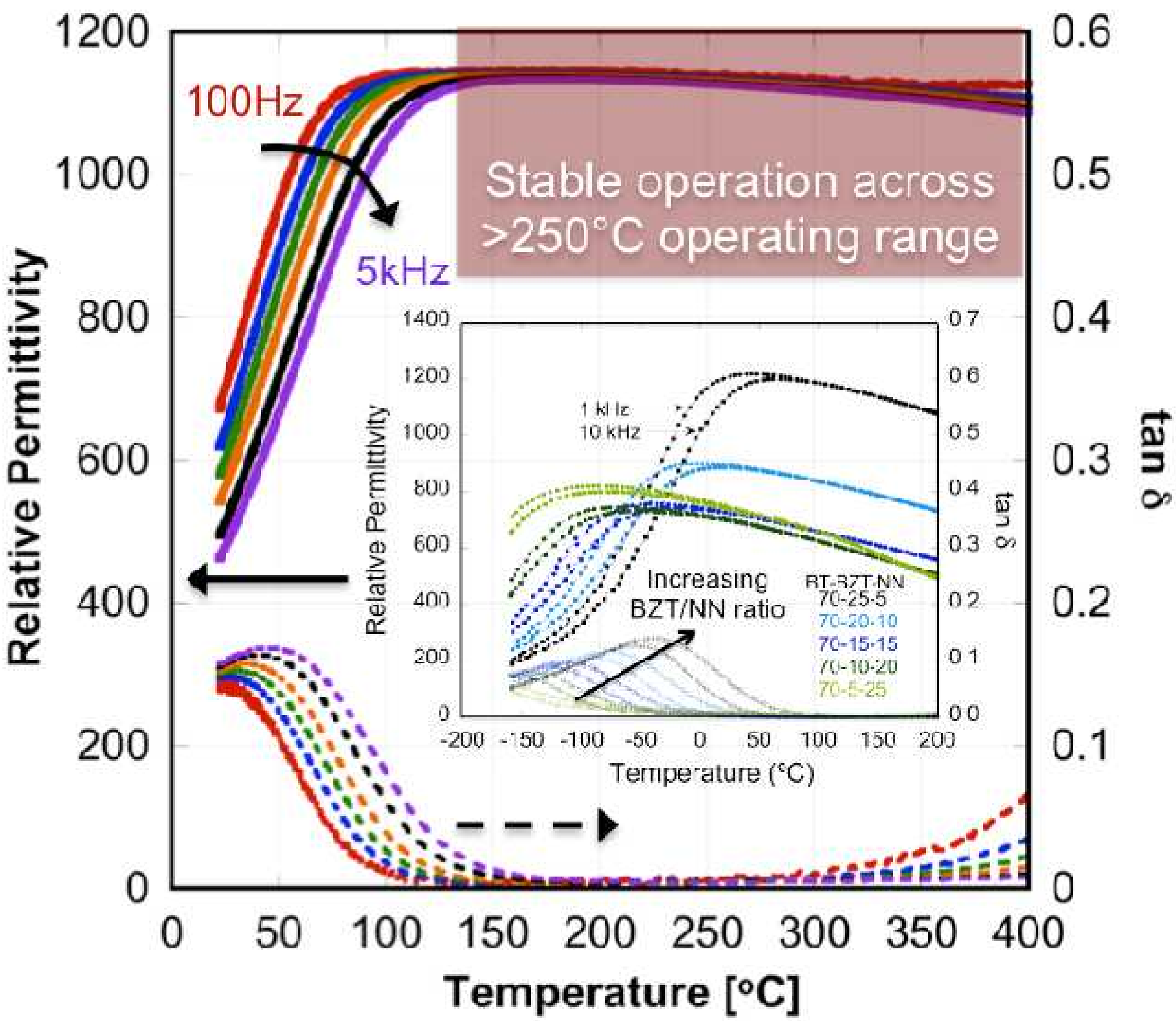
$$J = \int_0^{V_{max}} CV^2 \longrightarrow \int_0^{E_{max}} KE^2$$







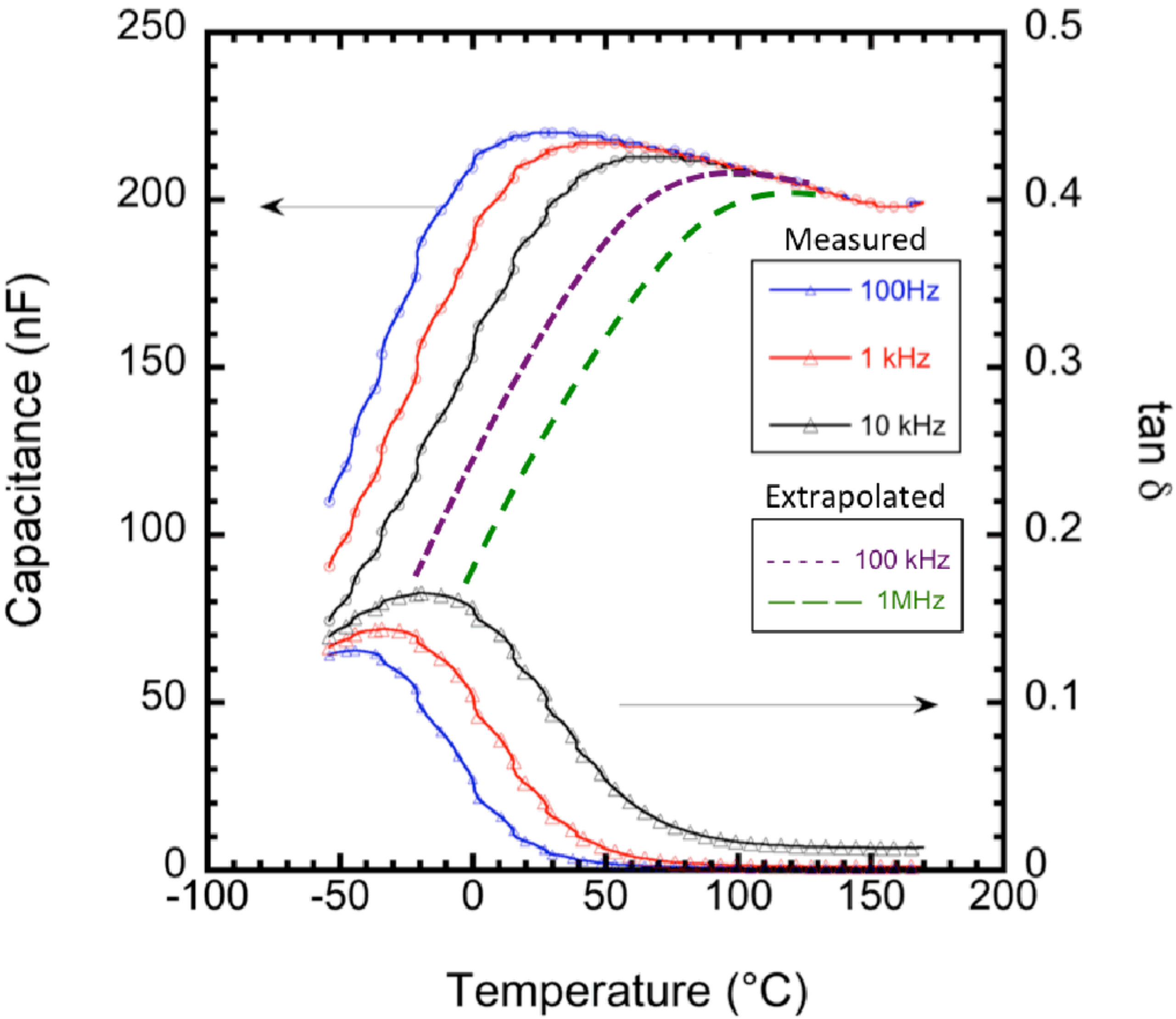
High Temperature Operation



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

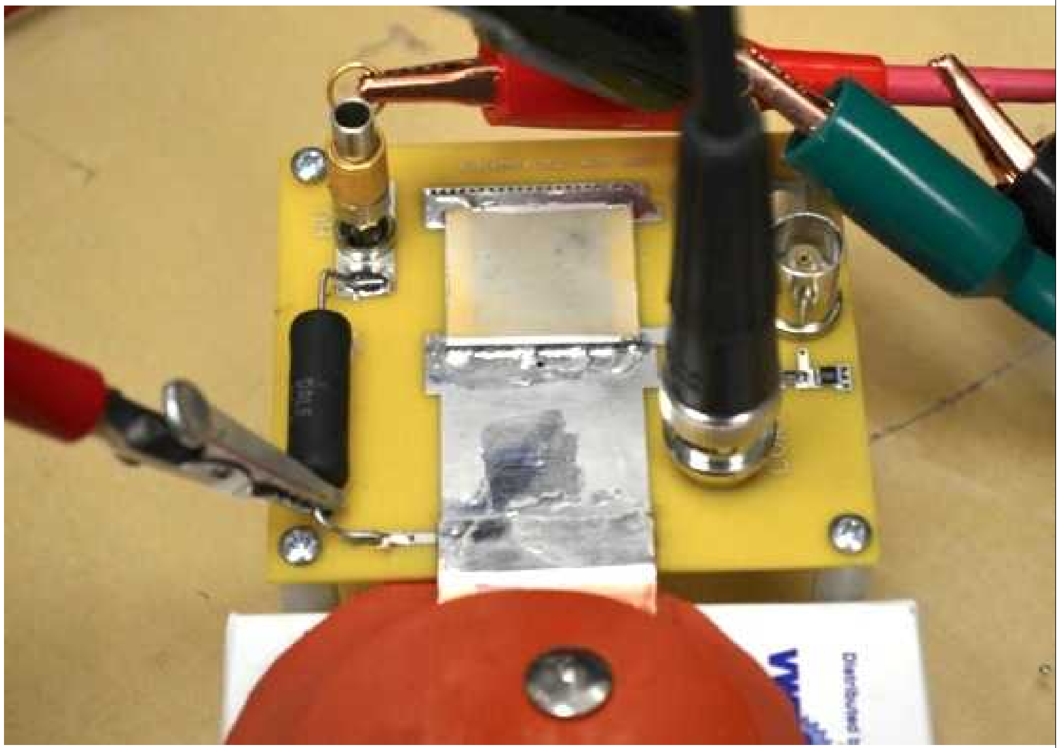
We can shift the temperature range for stable operation around by ~250°C via chemical modification *without sacrificing voltage stability*

Time Domain Performance



- Relaxor dielectrics exhibit characteristic frequency dispersion over relatively broad temperature ranges
- For pulse discharge or switched inverter applications that charge slowly and discharge quickly, which values are relevant?

Time Domain Performance



Low inductance board with compensated and calibrated CVR for pulse discharge (time domain) measurements

Large piezoelectric response of traditional relaxor ferroelectric causes fracture during such testing

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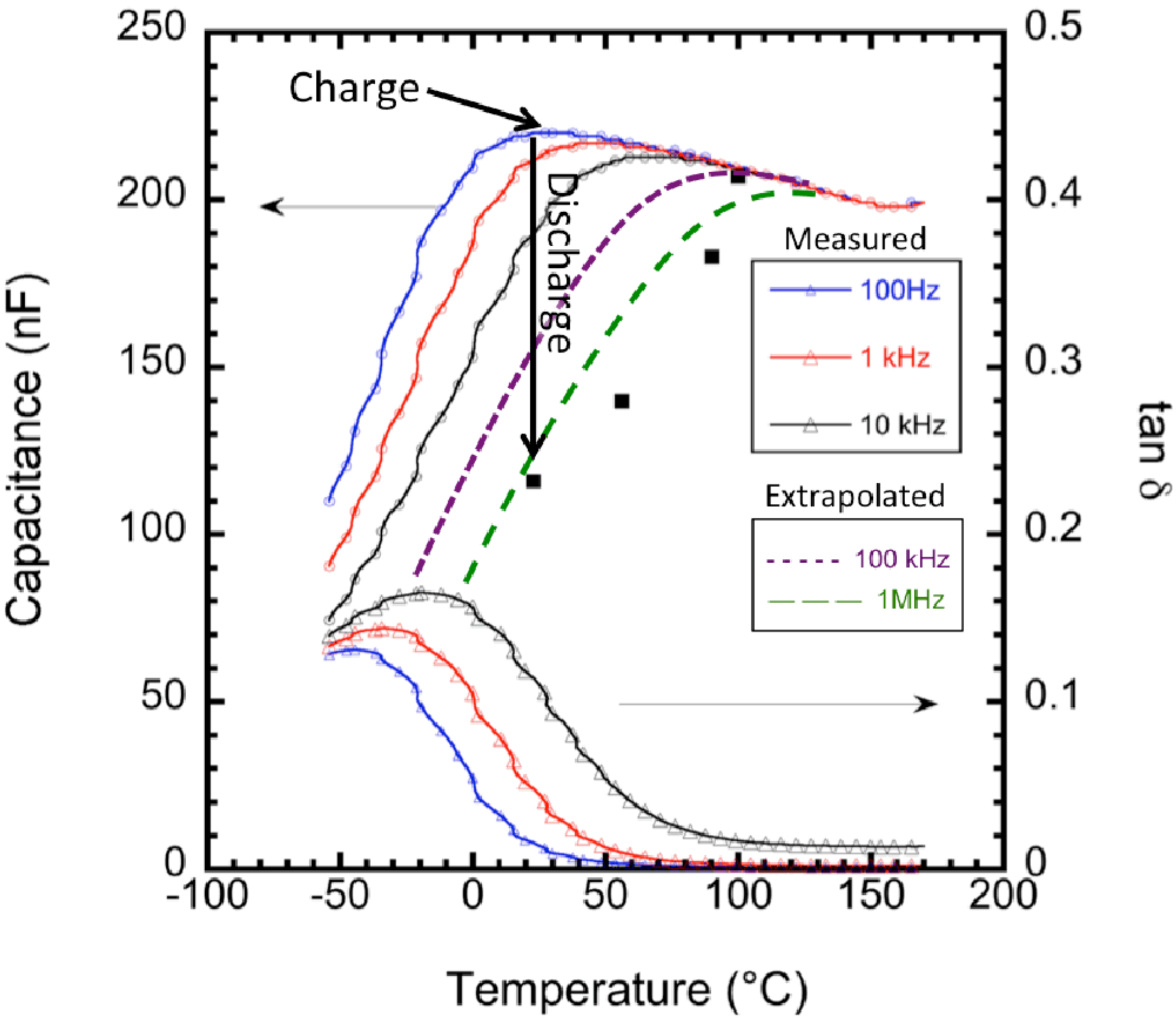
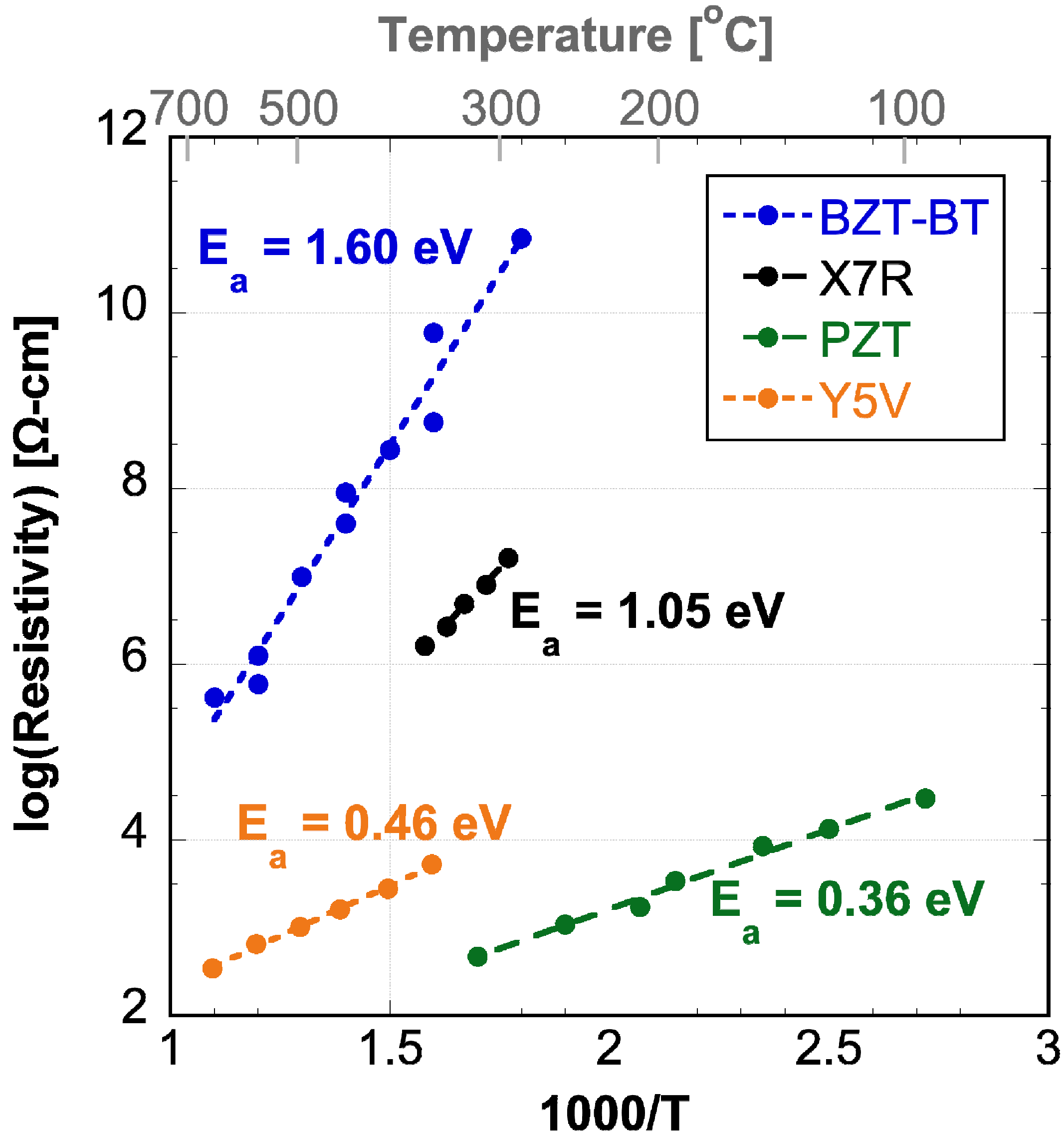
- Fitting critically damped discharge waveform allows determination of real part of permittivity

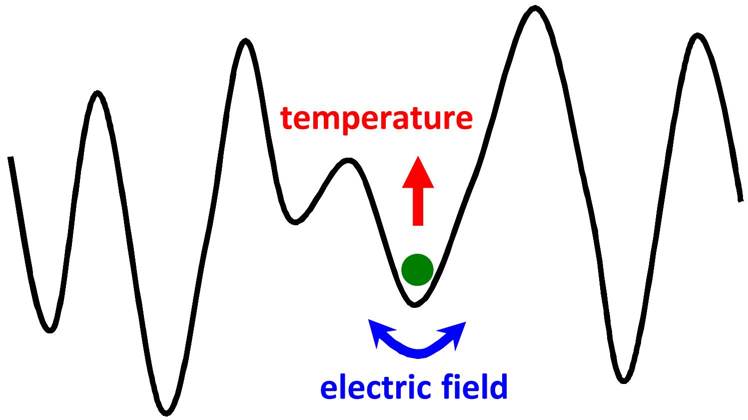
Time Domain Performance



- Discharge data correspond to frequencies from 2.0-2.8 MHz
- Direct time domain results correlate well with extrapolated frequency-domain curves
- First known confirmation of relaxor response in time domain

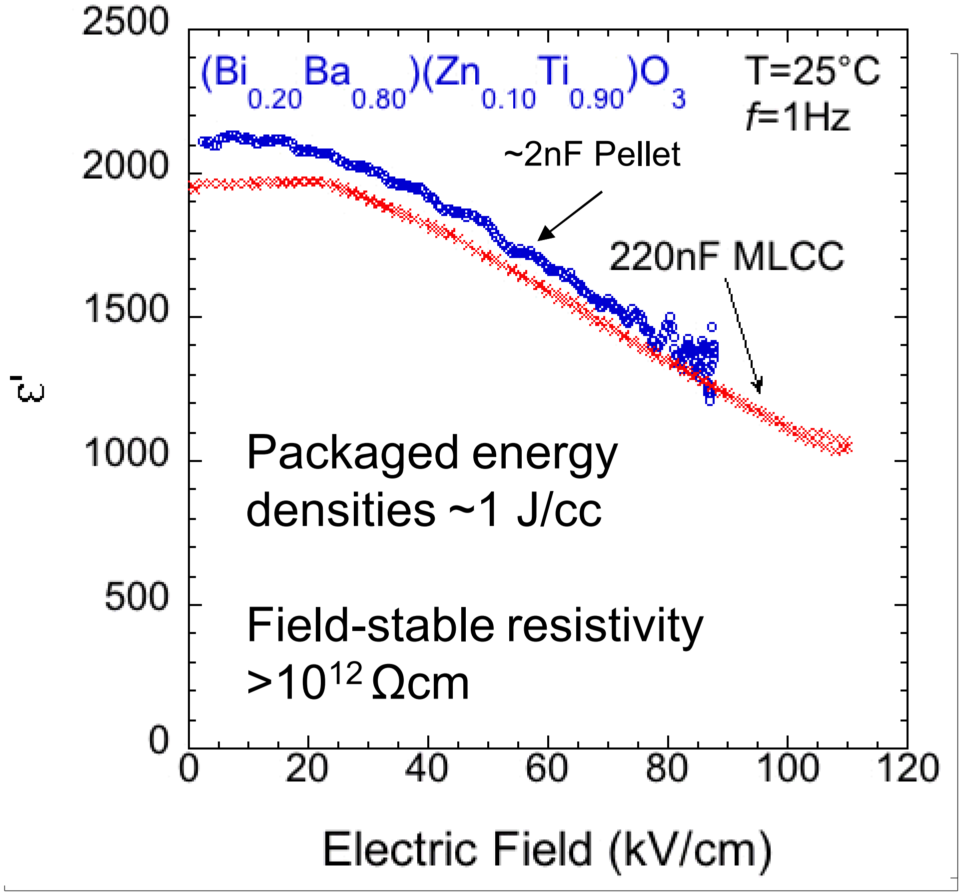
High dc Resistivity → Reliable





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

Prototype MLCCs: 200nF @ 1700V



Cast and co-fire with Pt @ 1040°C

- Maintain RC time constants >200 sec even at >60kV/cm, >150°C (likely higher)
- Smaller samples tested under harsher conditions maintain RC >100 sec >350°C
- Mechanism(s)??

MLCC dielectric exhibits high-Z core

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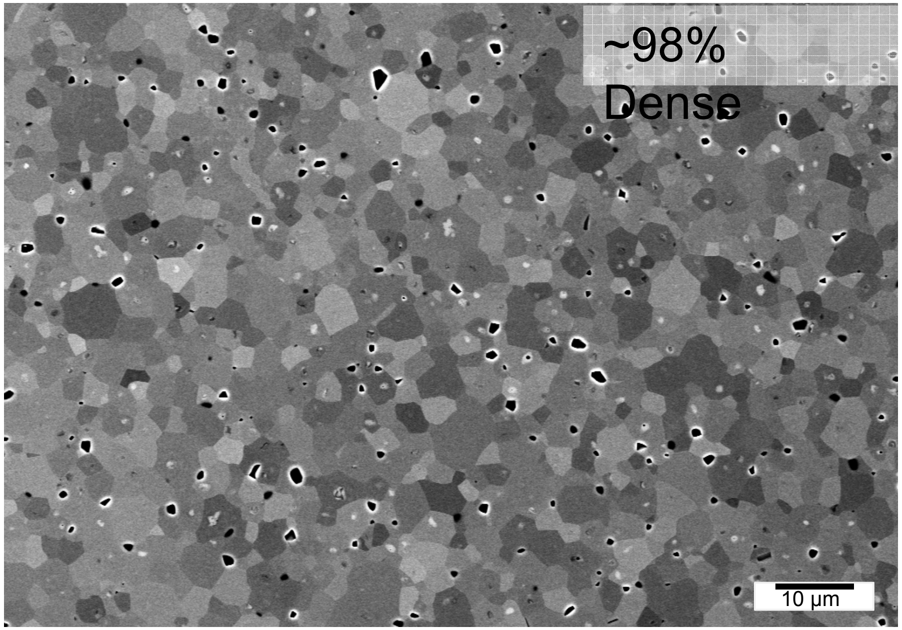
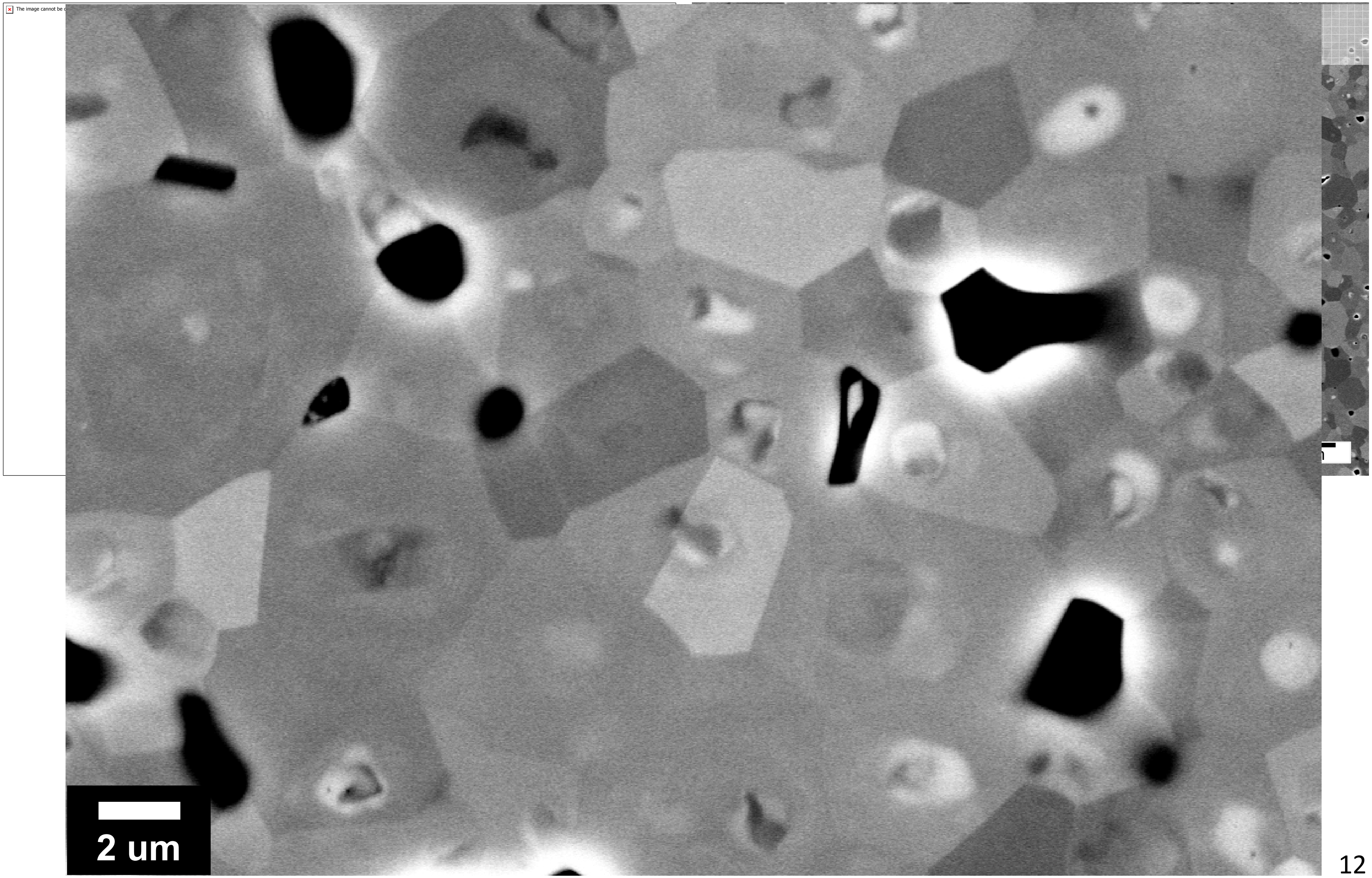
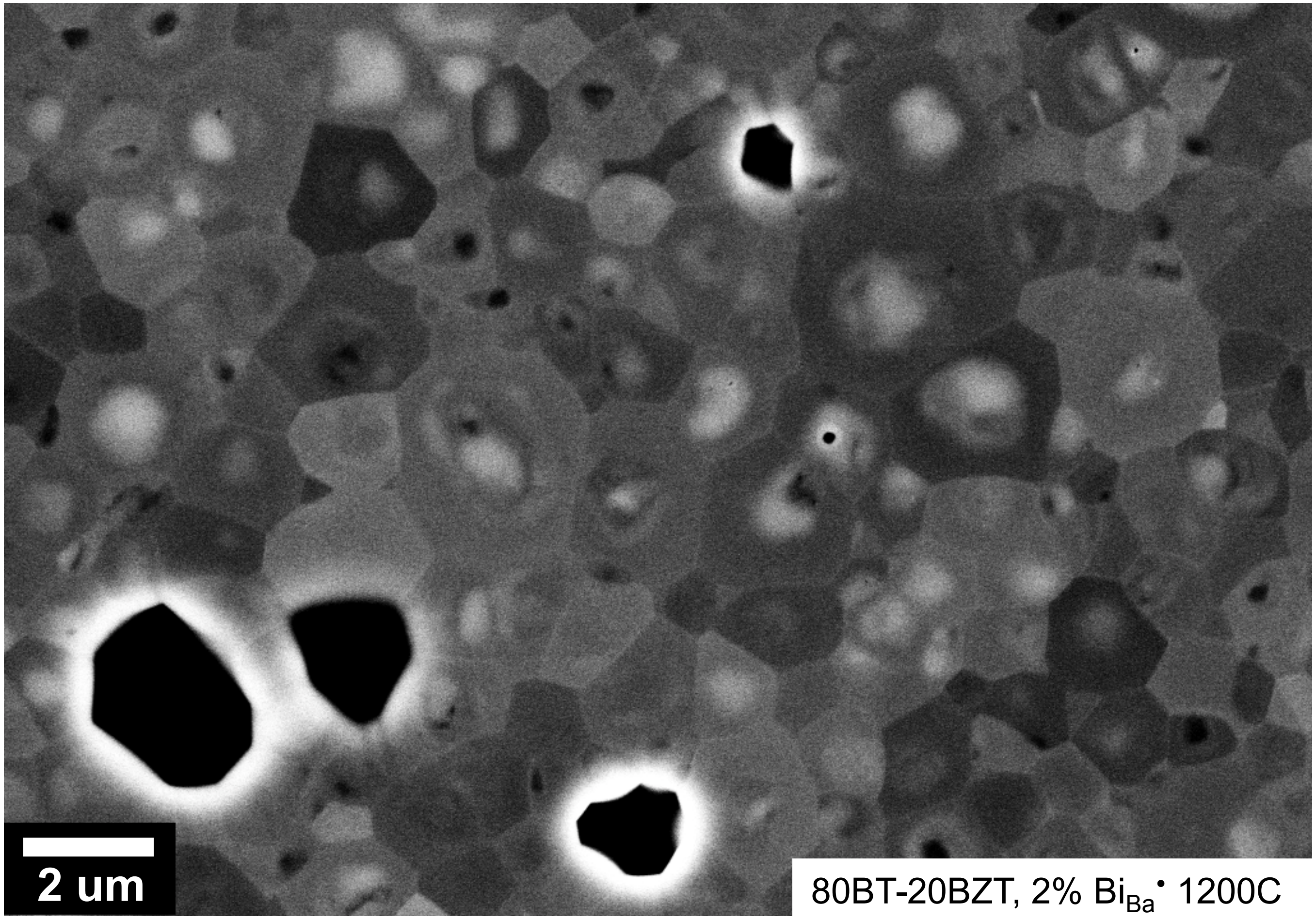


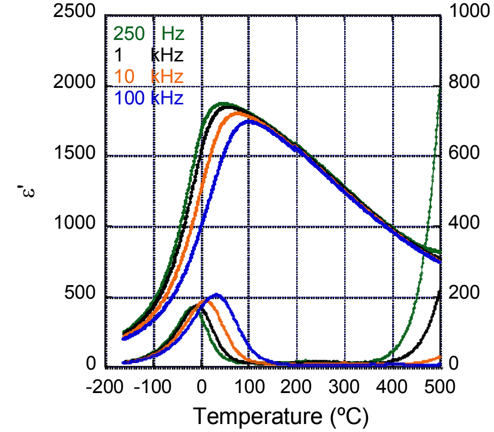
MLCC dielectric exhibits high-Z core

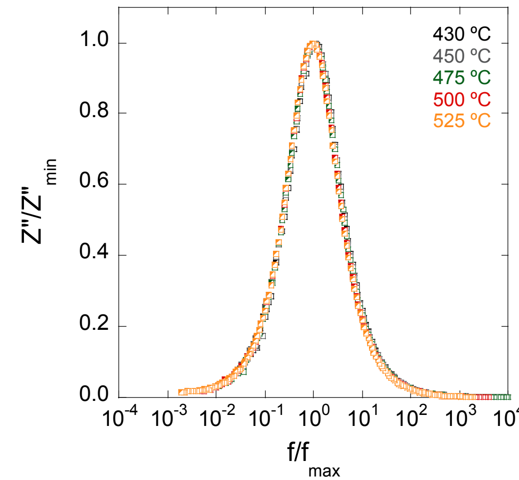


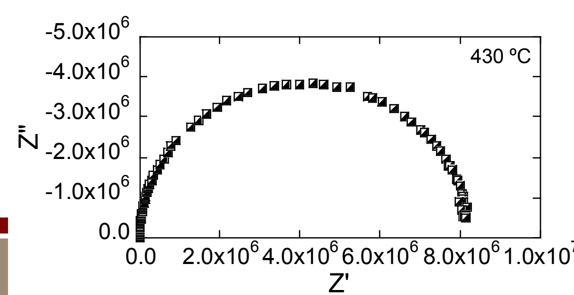
Donor-doped

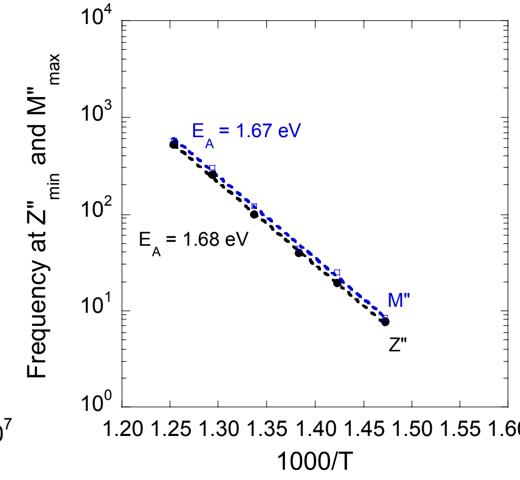


80BT-20BZT, 2% $Bi_{Ba}^{\bullet}$ 1200C

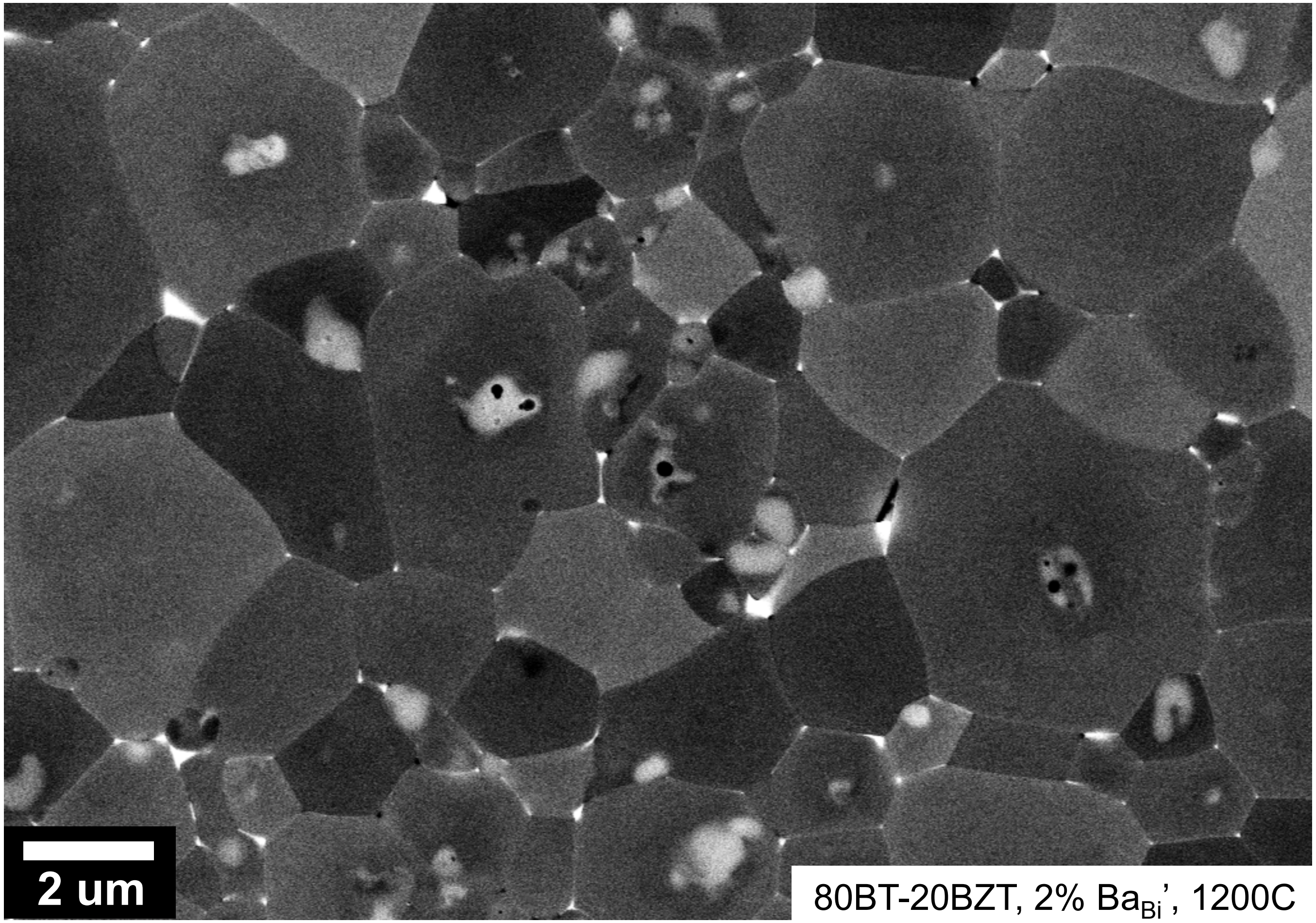


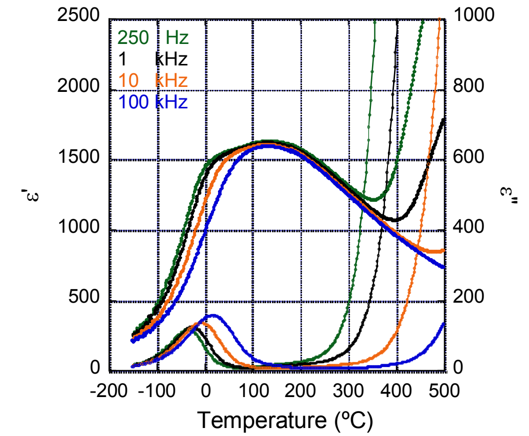


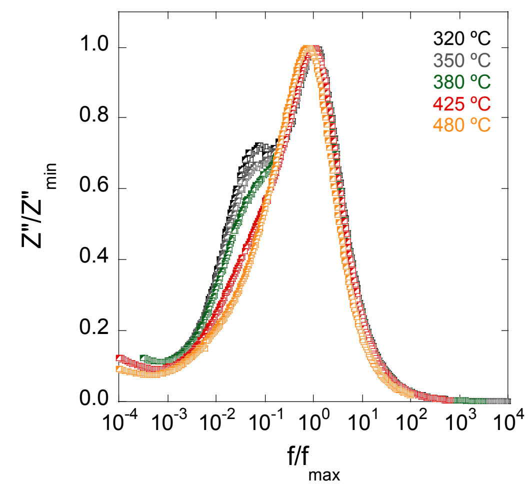


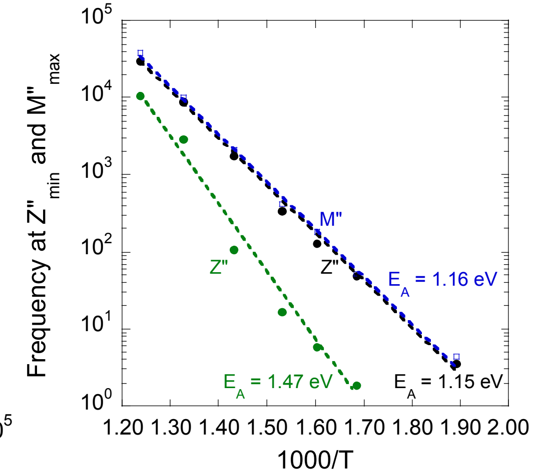


Acceptor-doped

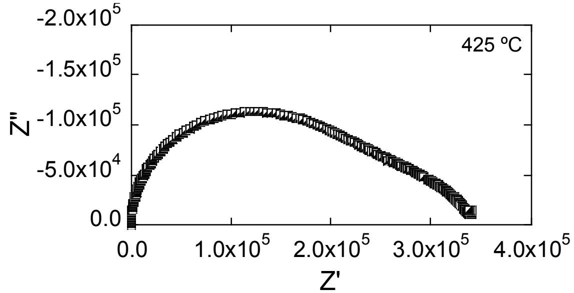




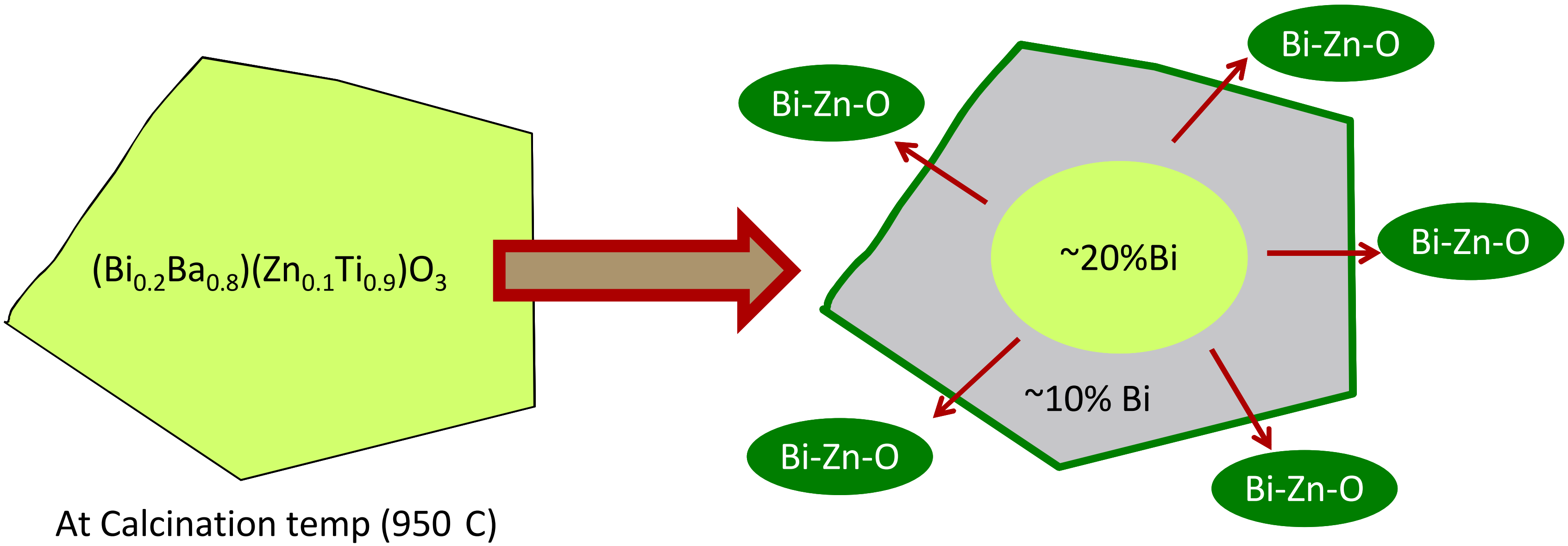


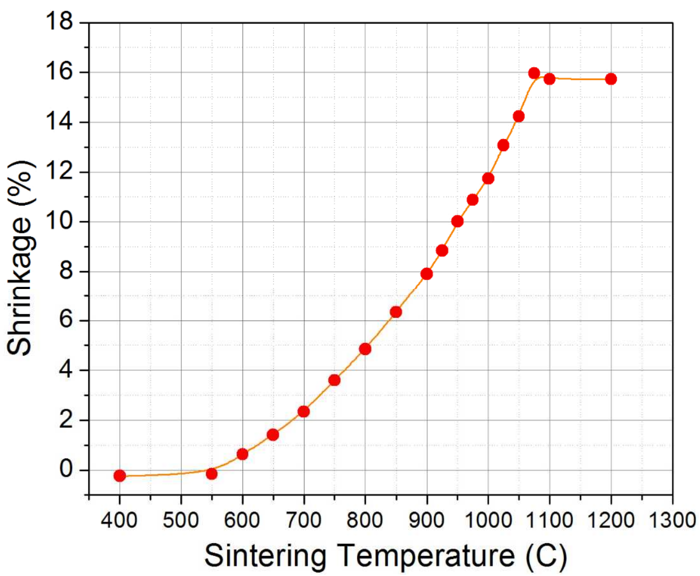


80BT-20BZT, 2% Ba_{Bi}', 1200C



Calcination



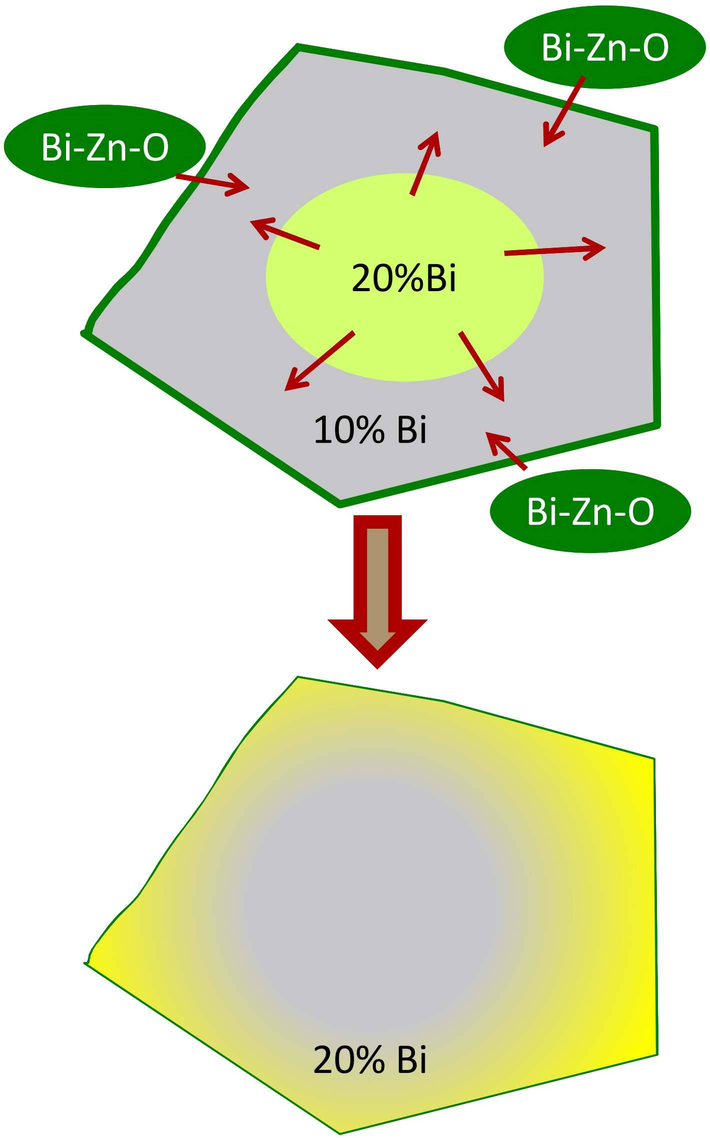


Working assumption is that the equilibrium solubility of Bi_2O_3 in $BaTiO_3$ is breached upon cooling.

On cooling from 950 C, Bi exsolves from perovskite solid solution, leading to Bi-rich core and Bi-Zn-O glassy phase at particle surfaces.

Initial sintering occurs as Bi-Zn-O phase melts.
Next step depends on **dominant defect species.**

Sintering: Donor doped



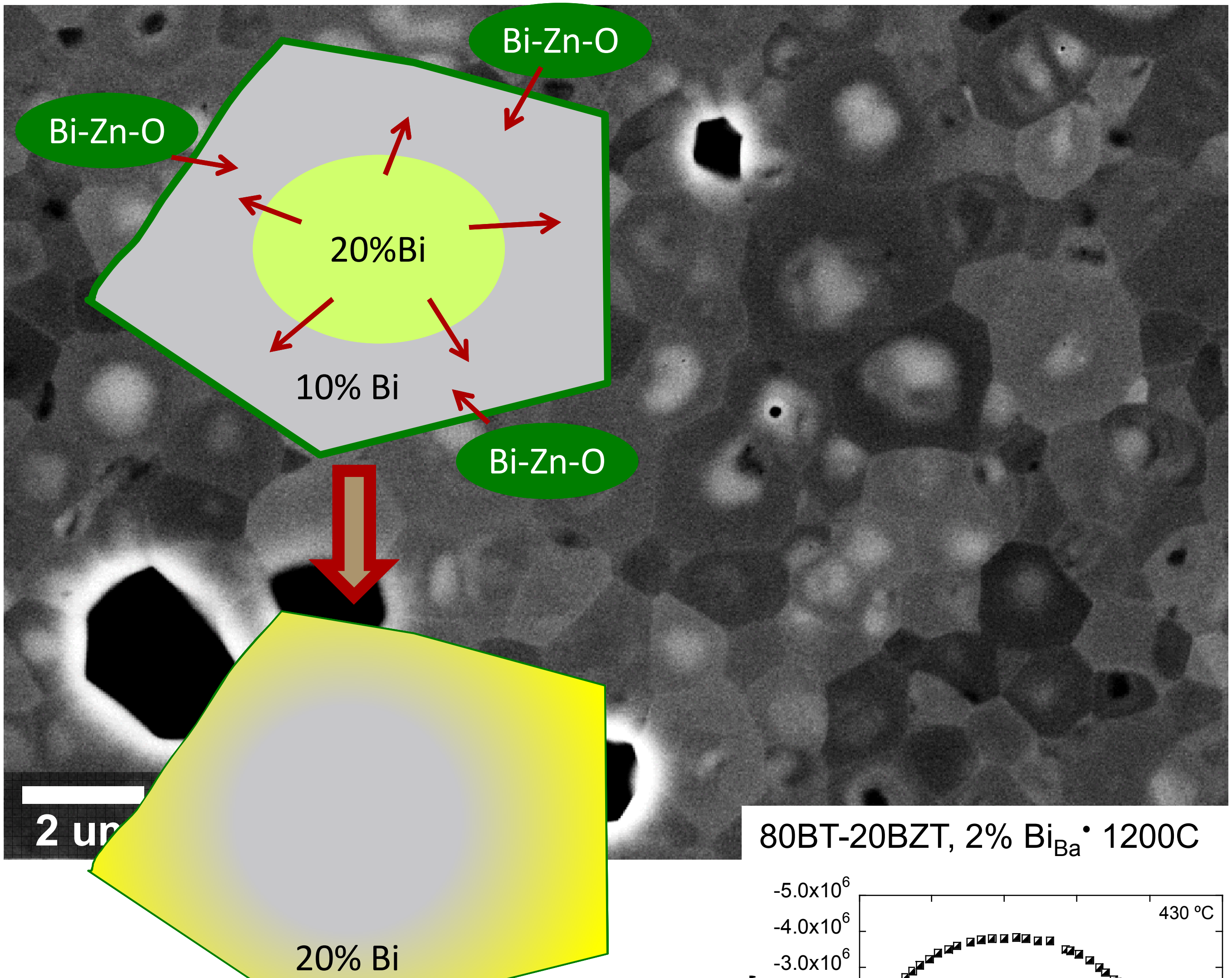
Donor Doped: Cation Vacancies Dominate

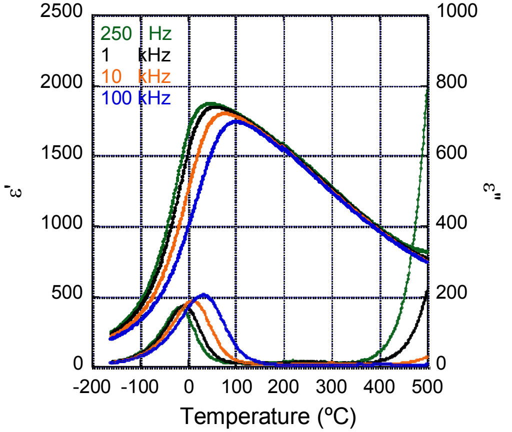
- Bi diffuses in from g.b., out from core
- Diffusion **assisted** by cation vacancies

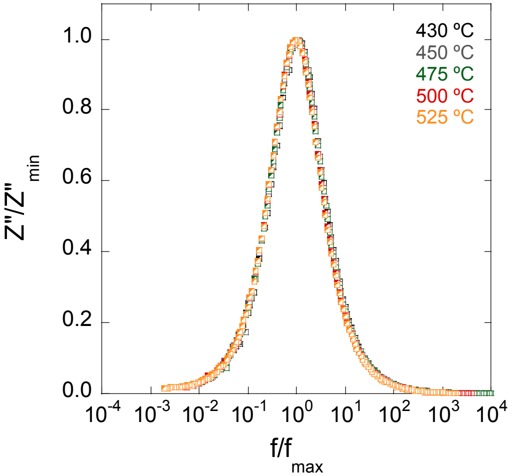
Resultant Microstructure

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

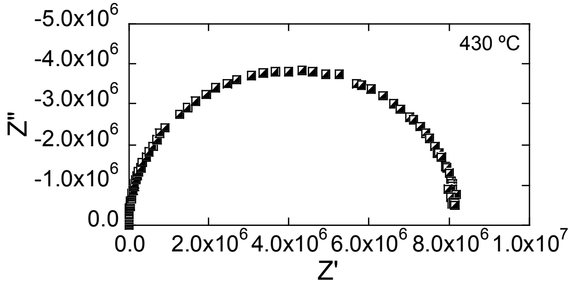
Sintering: Donor doped

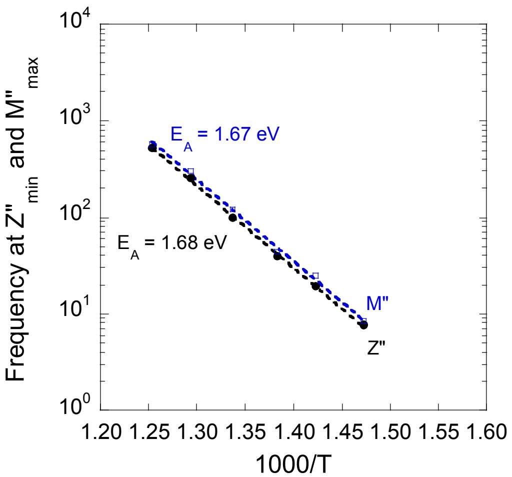




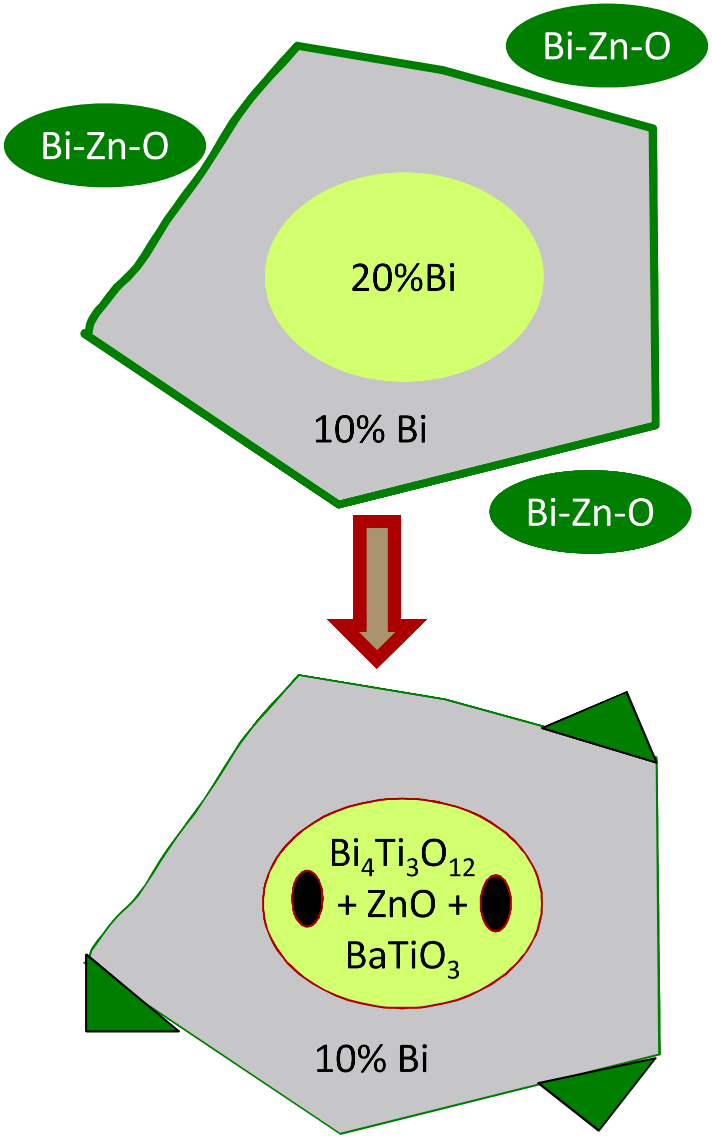


80BT-20BZT, 2% Bi$_{Ba}^{\bullet}$ 1200C





Sintering: Acceptor doped



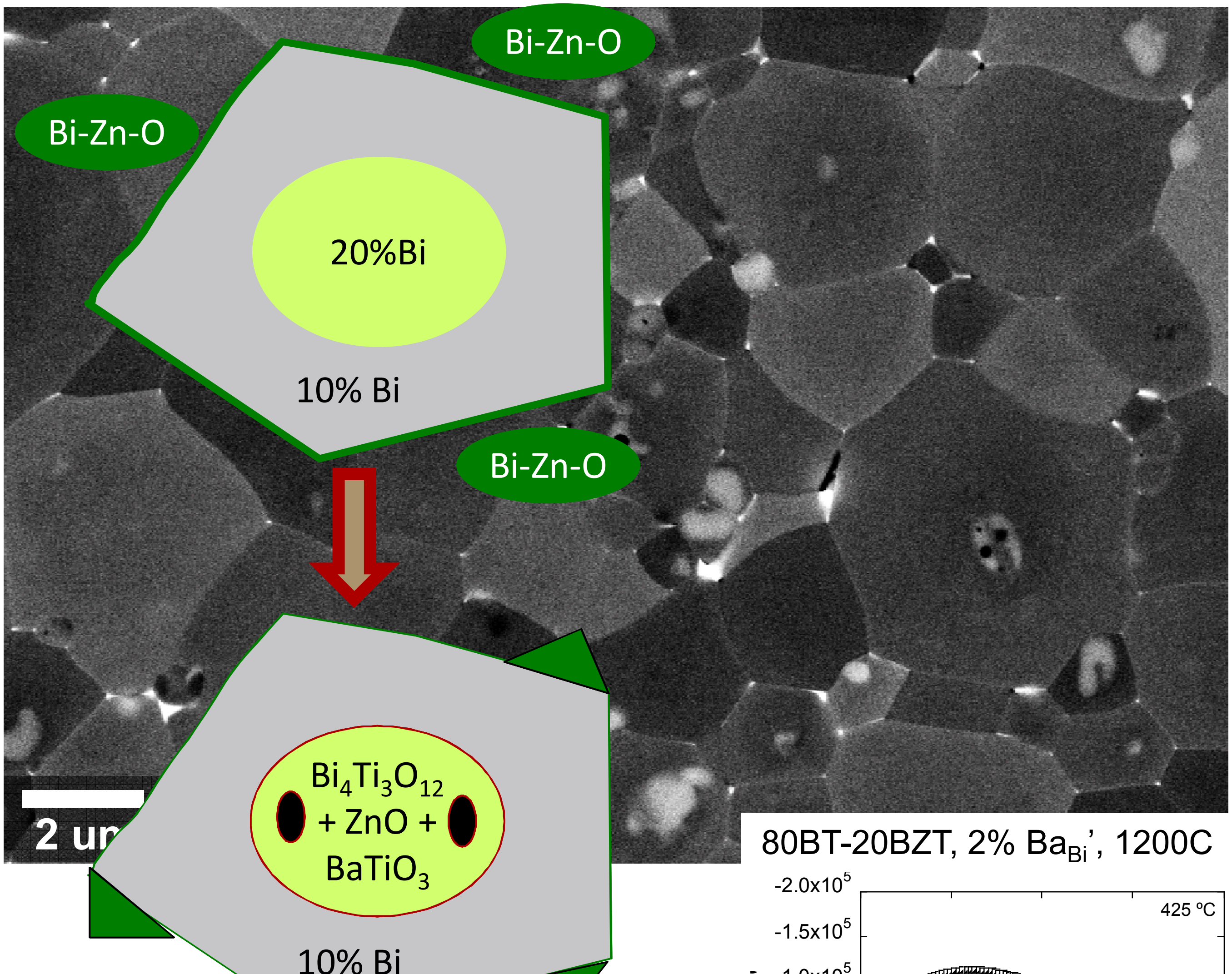
Acceptor Doped: Oxygen Vacancies Dominate

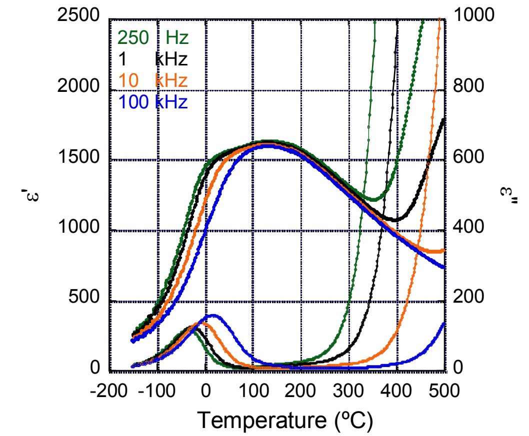
- Bi diffuses in from g.b., out from core
- Diffusion **inhibited** by lack of cation vacancies
- Bi-rich phase at triple points
- Bi-rich cores decompose into equilibrium phases: $Bi_4Ti_3O_{12}$ + ZnO + Ba-Ti-O

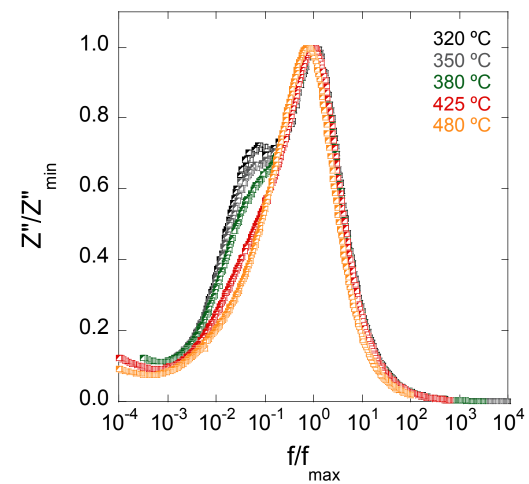
Resultant Microstructure

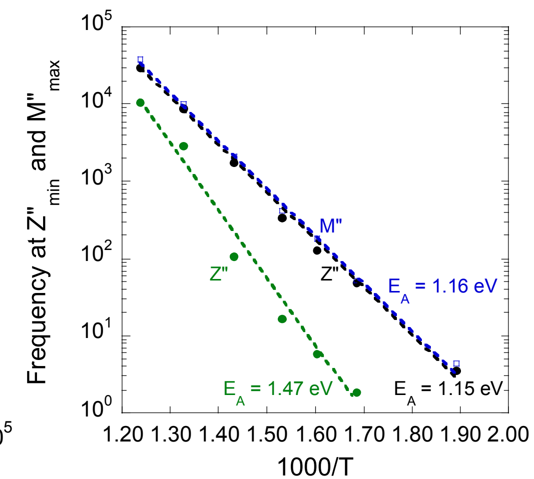
- High-Z phase at triple points
- Well defined core boundary
- Low-Z precipitates in core region
- Electrically heterogeneous microstructure (two relaxations)

Sintering: Acceptor doped

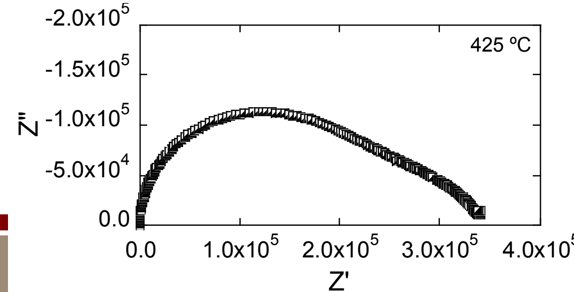






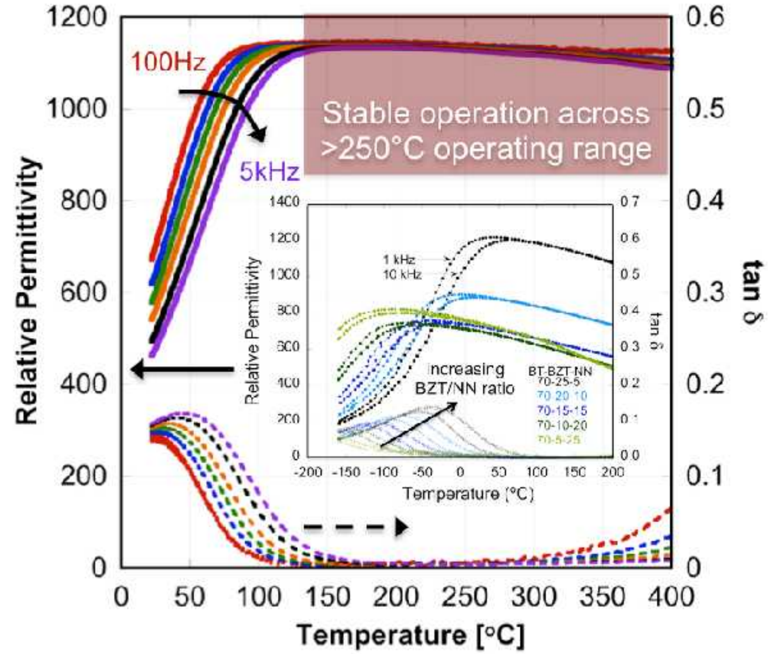


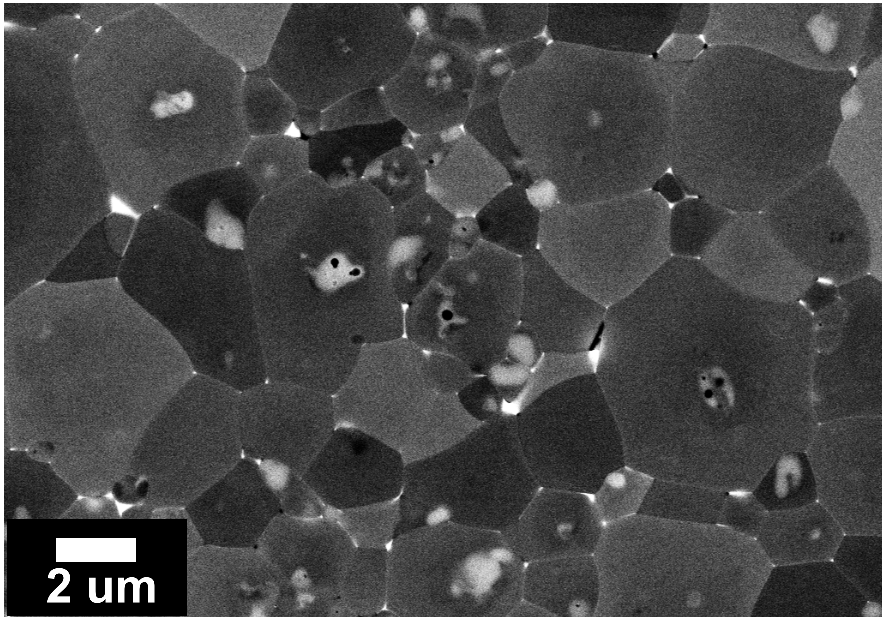
80BT-20BZT, 2% Ba_{Bi}', 1200C

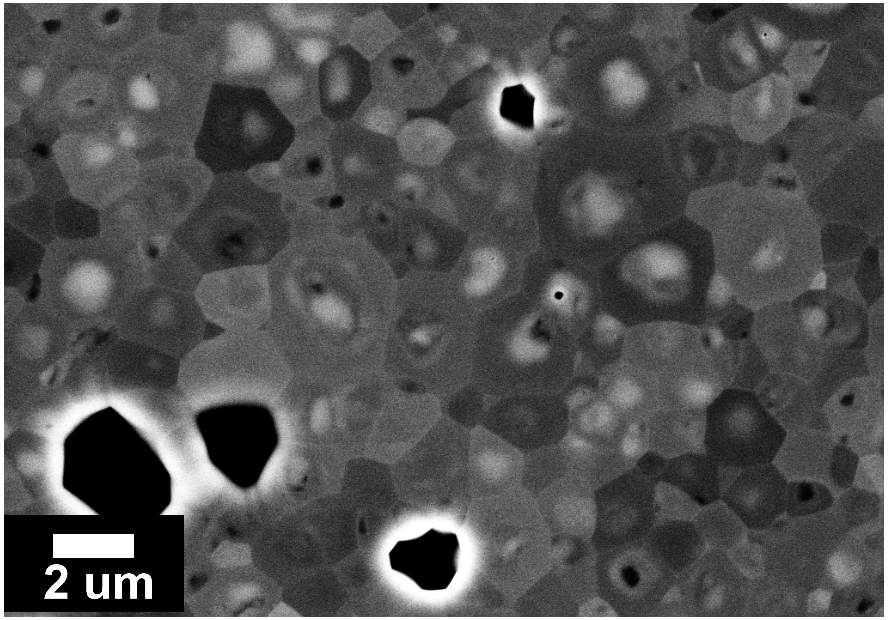


Summary

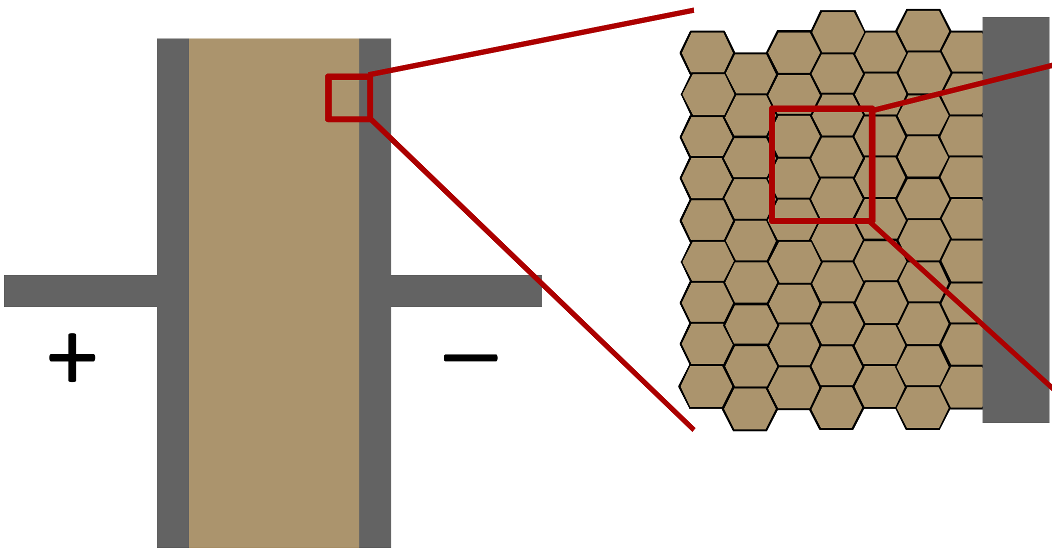
- Fabricated high energy density dielectrics with temperature- and voltage-stable performance
- Defect chemistry has strong influence on microstructure as well as electrical response

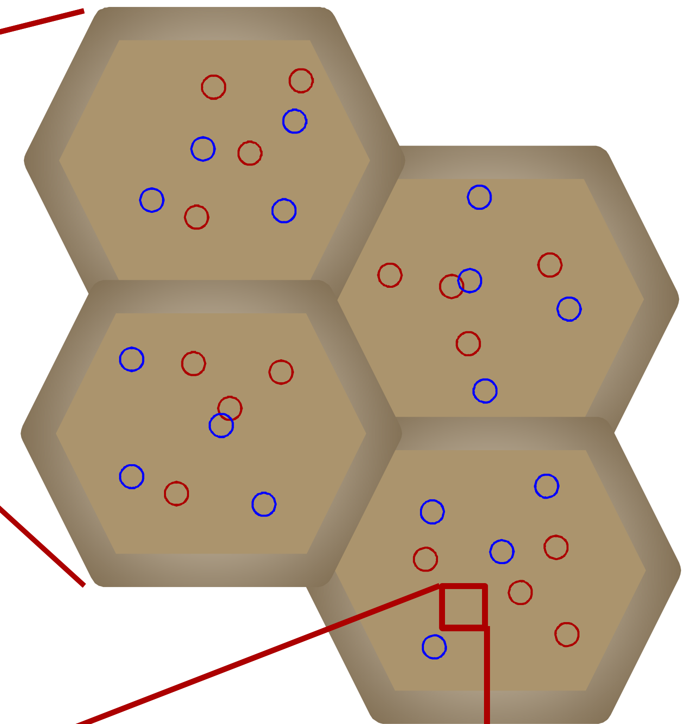


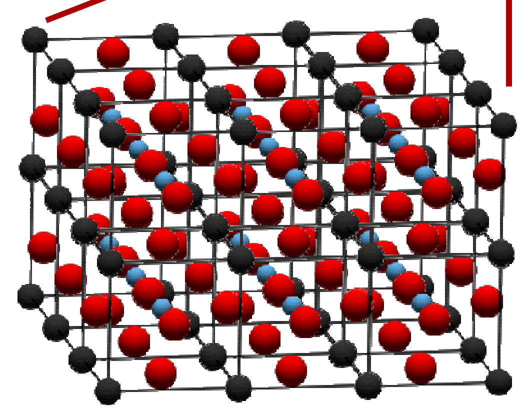




Degradation in Ceramic Dielectrics



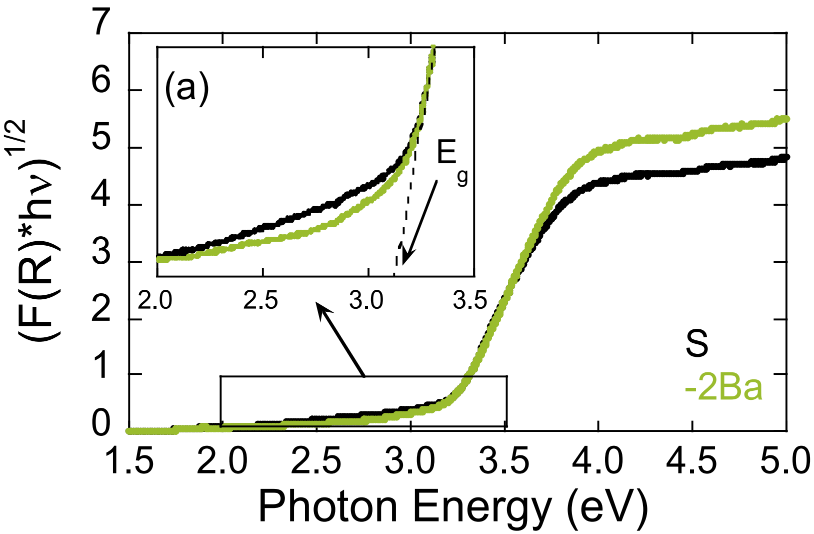


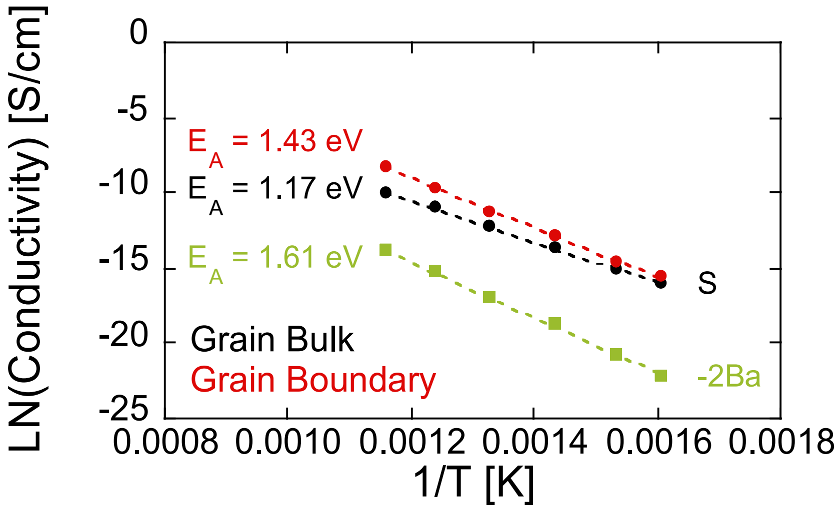


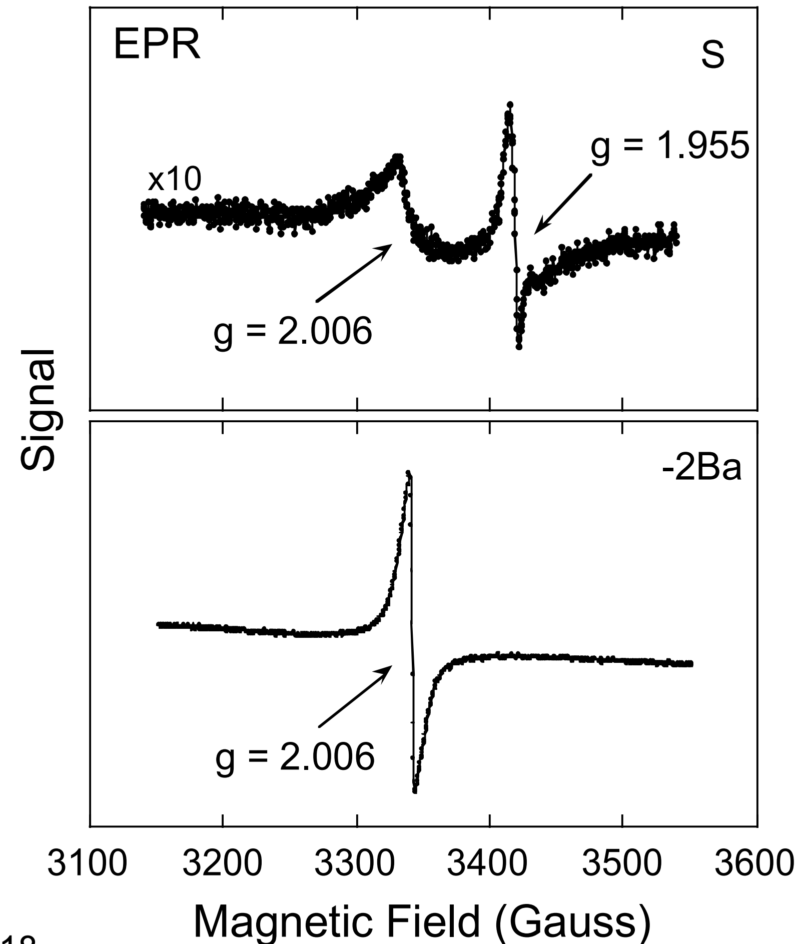
- Long-term degradation generally due to migration of charged ionic defects
- HALT and MTTF prediction require quantitative description of mechanisms

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

Defects: Optical & Electrical Info



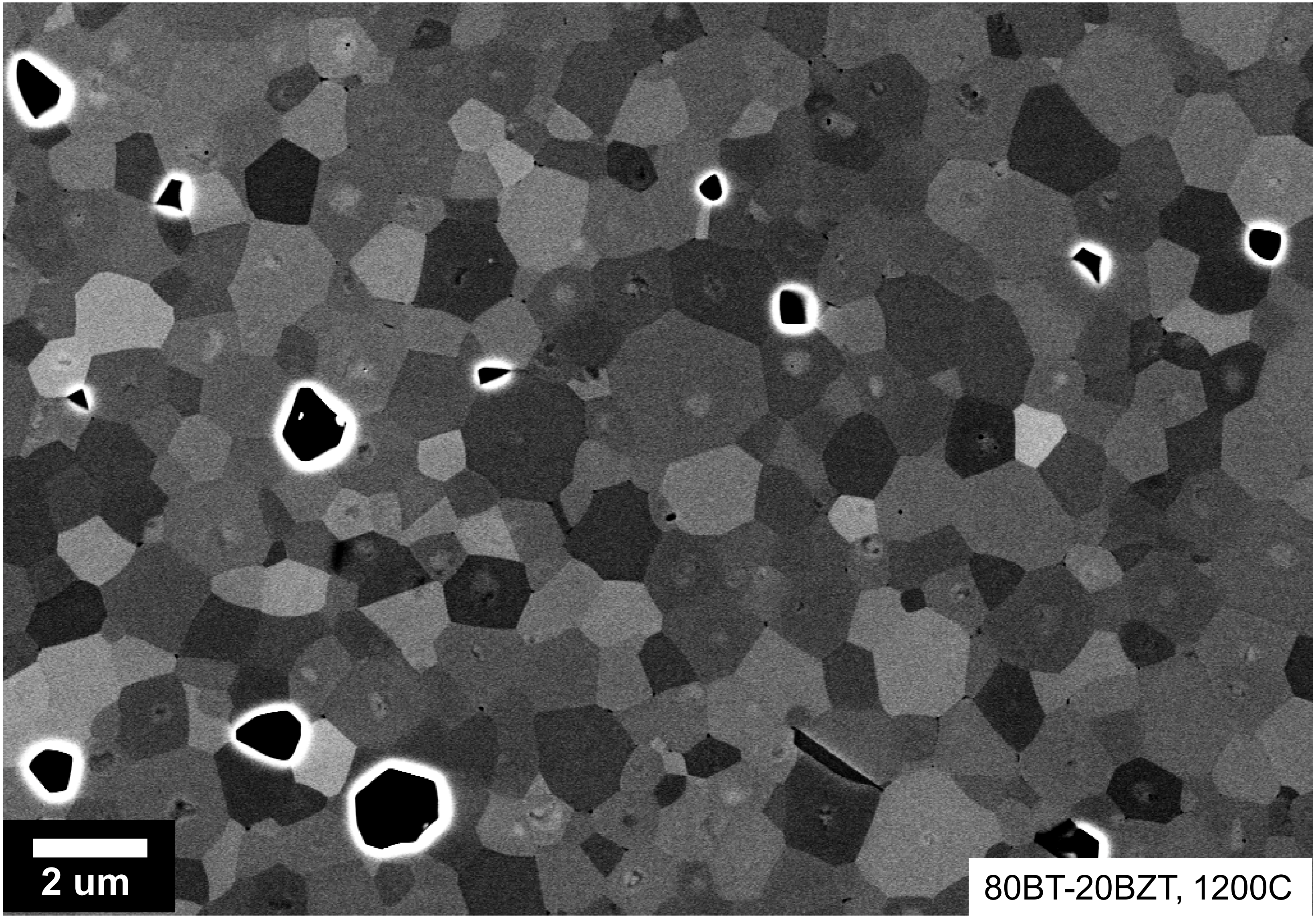




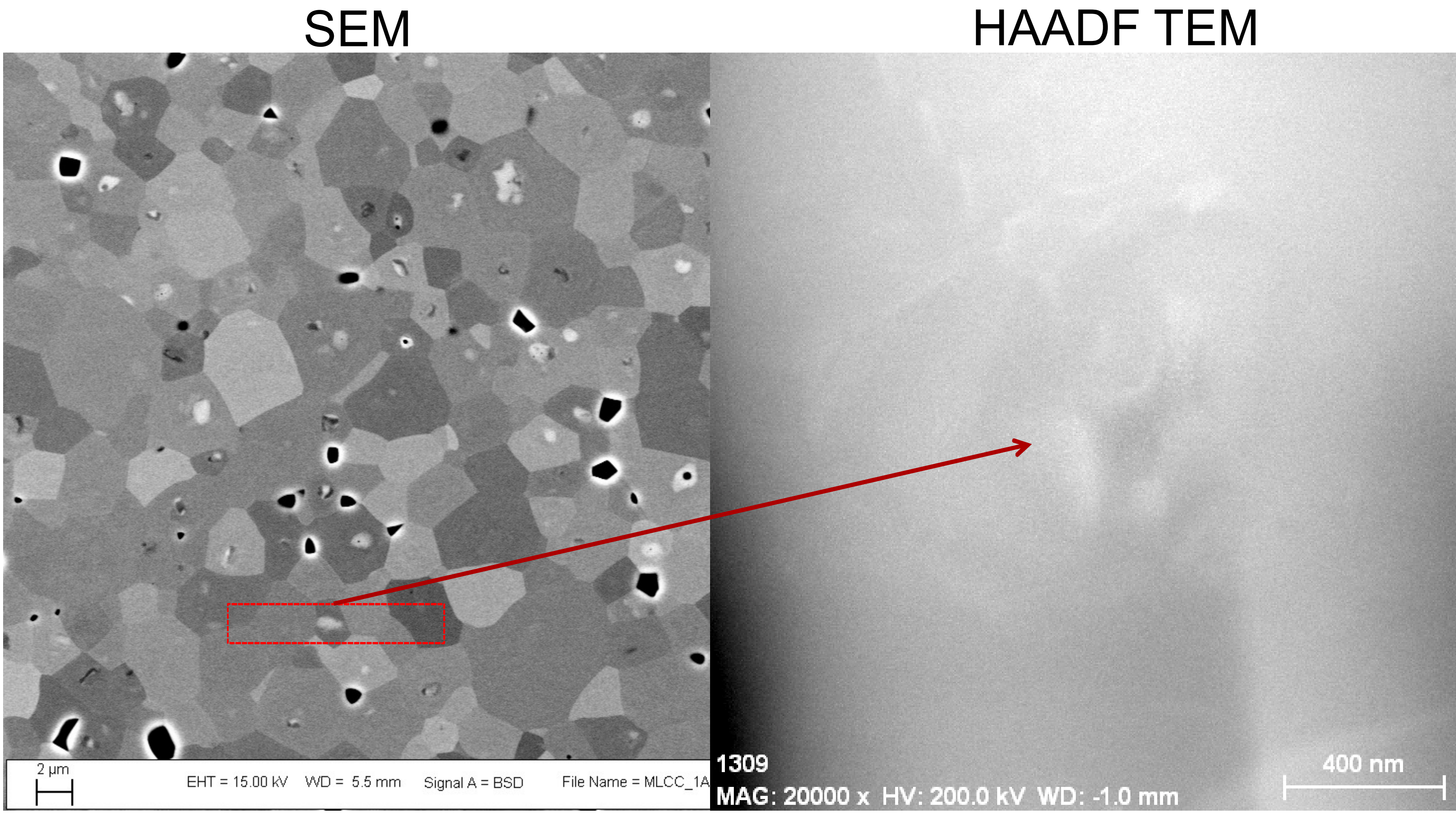
Raengthon, et al., Appl. Phys. Lett. (2012)

- Defect studies suggest V_{Ba}'' – V_O^{oo} pairs are strong carrier traps

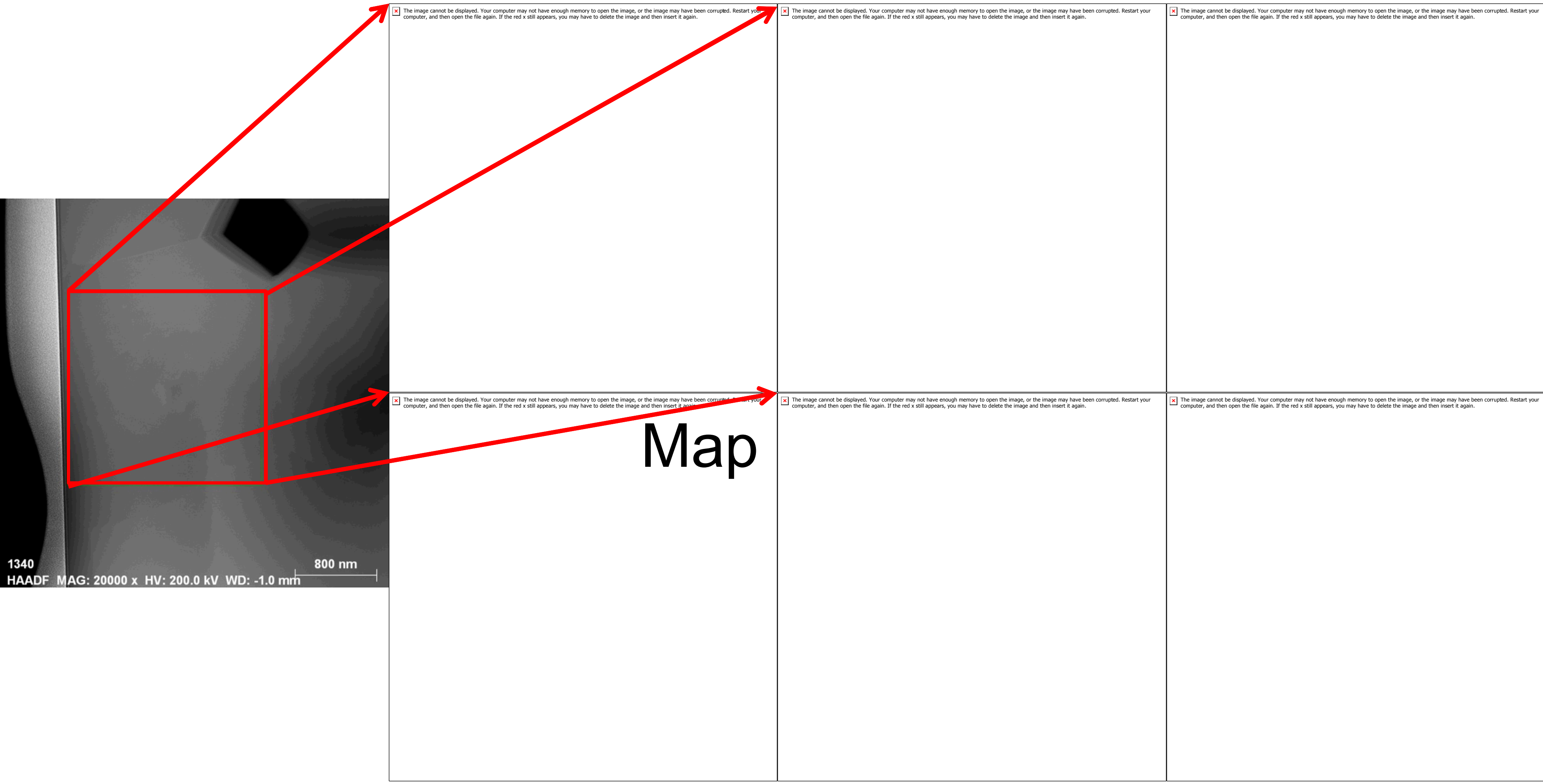
Well-Polished Section, Channeling



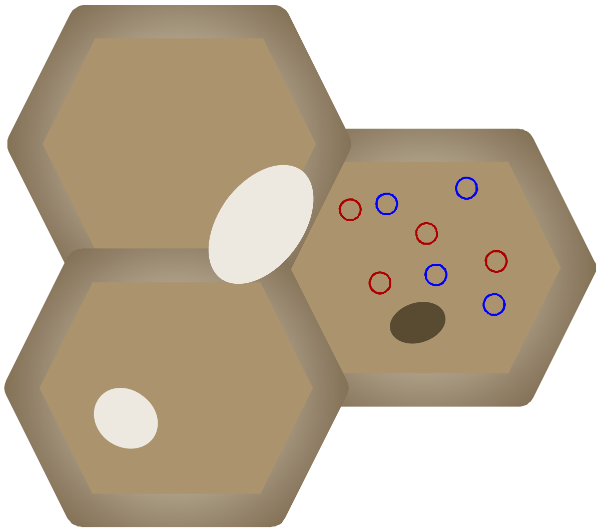
Compositional Variation

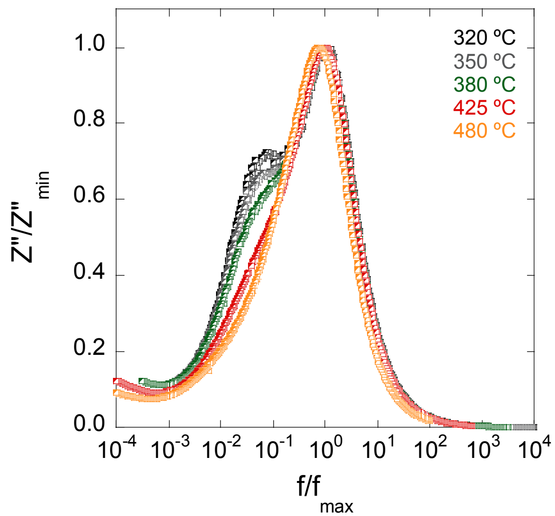


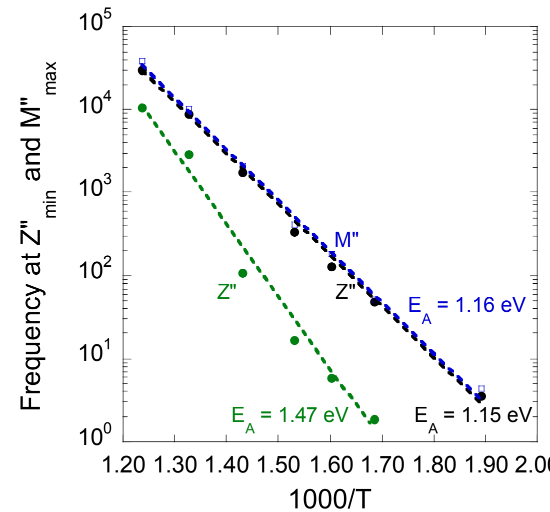
Bi and Zn Co-segregation

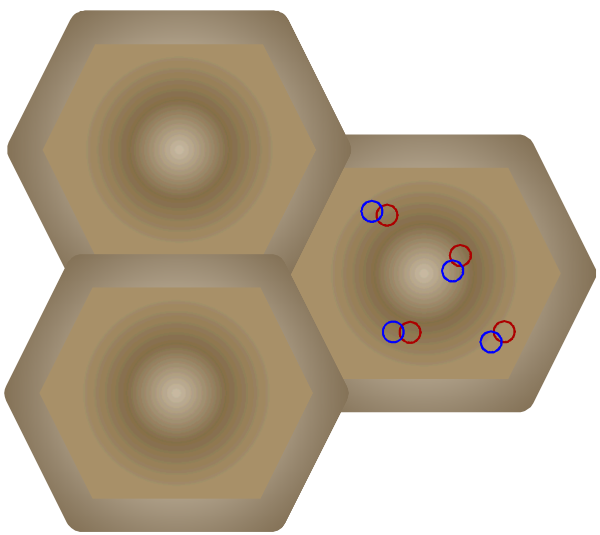


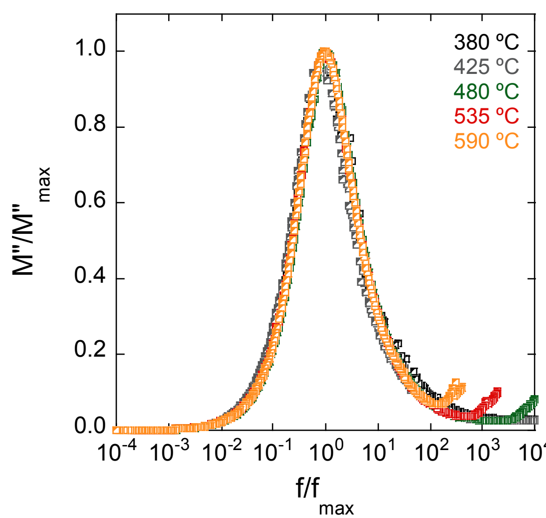
Microscale Heterogeneity

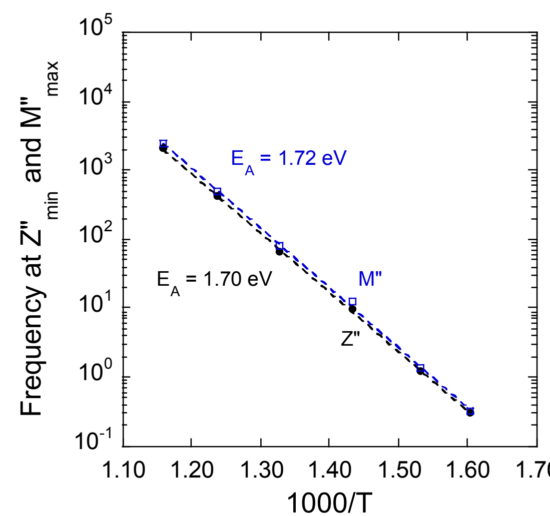












with Prof. David Cann, Oregon State University