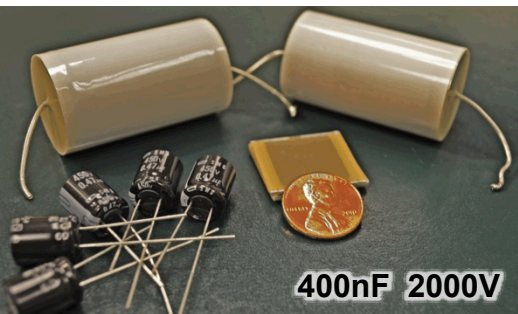
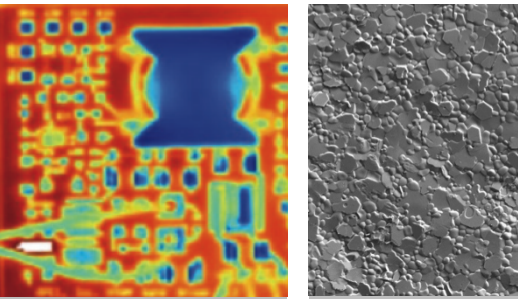


# Processing of $\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ - $\text{BaTiO}_3$ dielectrics for reliable high field operation

*or: what you don't know can't hurt you... can it?*



Geoff Brennecka, Harlan Brown-Shaklee and Mia Blea  
Sandia National Laboratories

Natthaphon Raengethon and David Cann  
Oregon State University

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

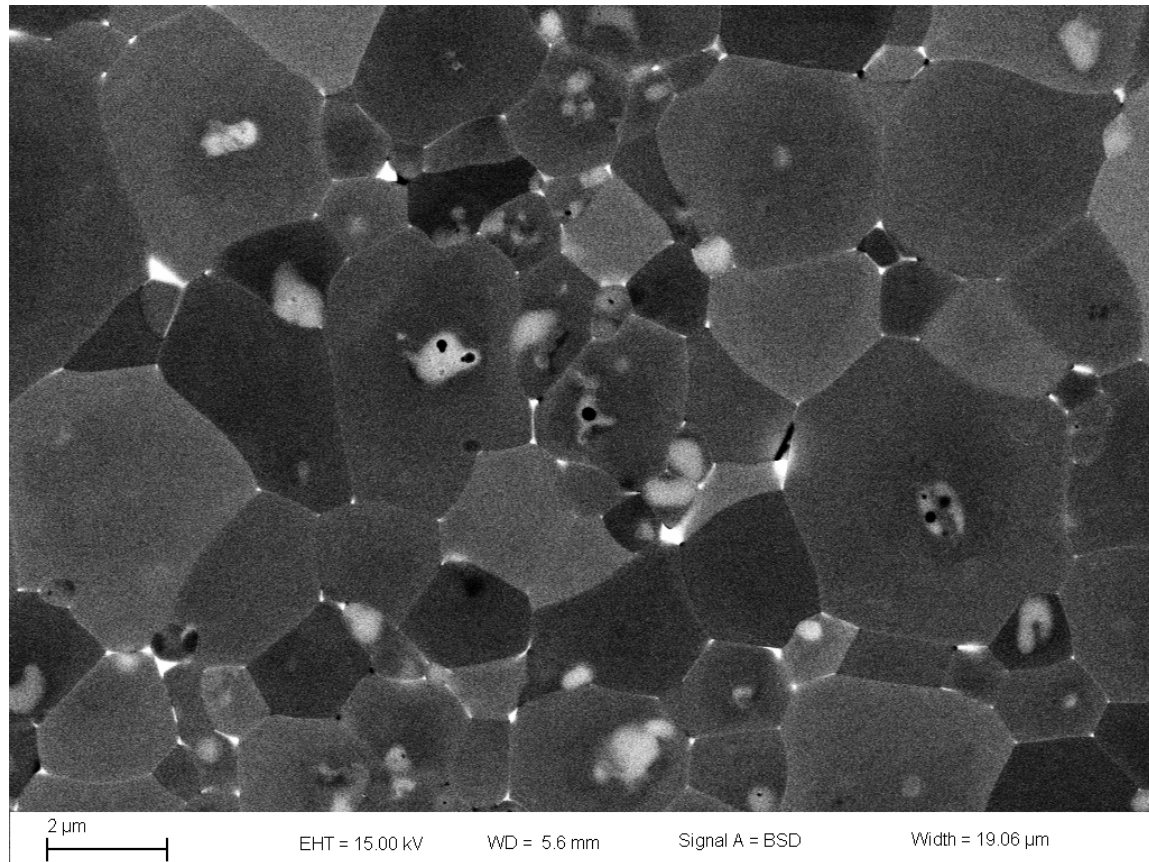


*Exceptional  
service  
in the  
national  
interest*

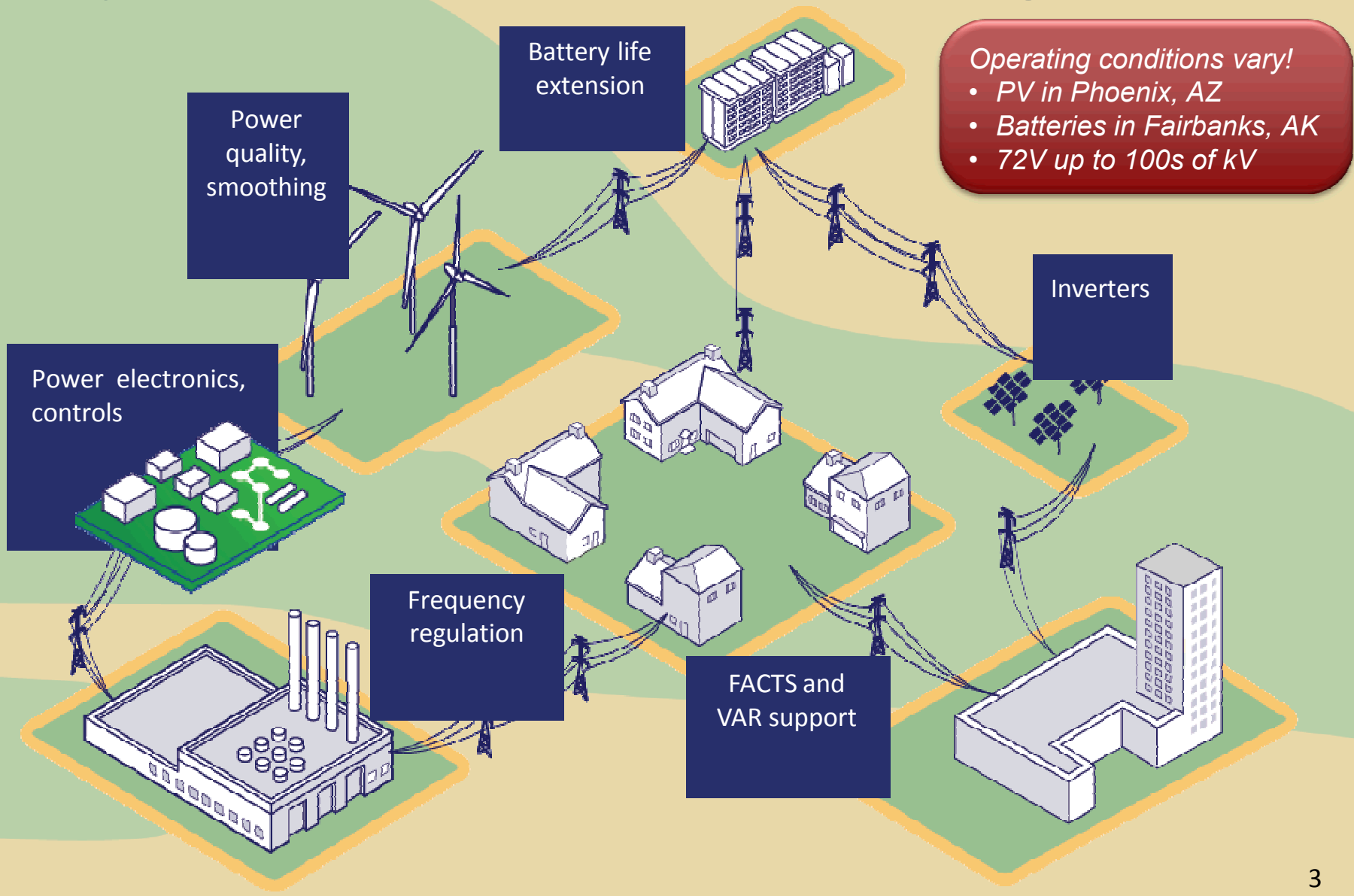


# Acknowledgements

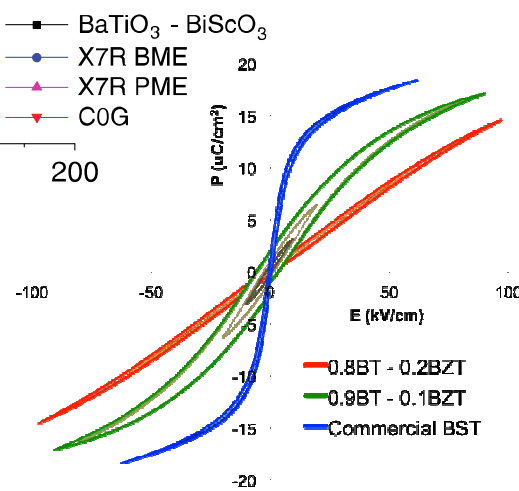
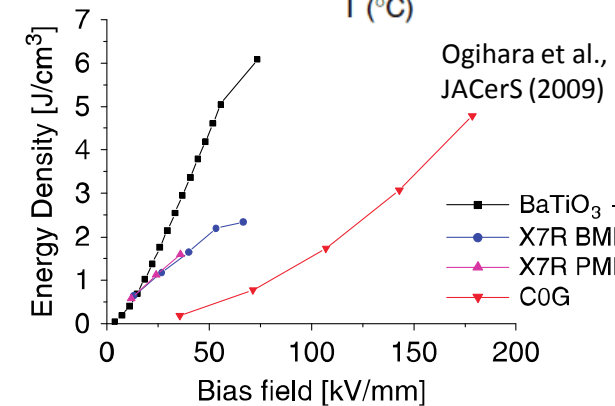
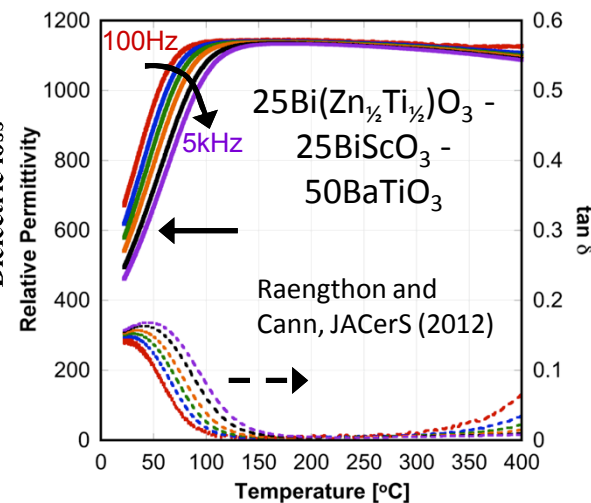
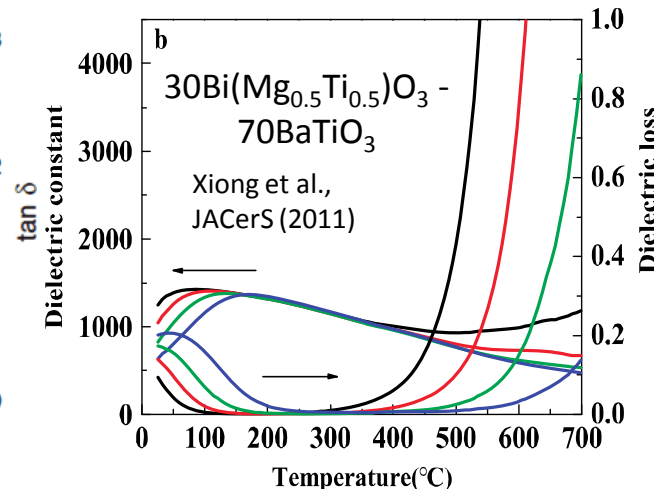
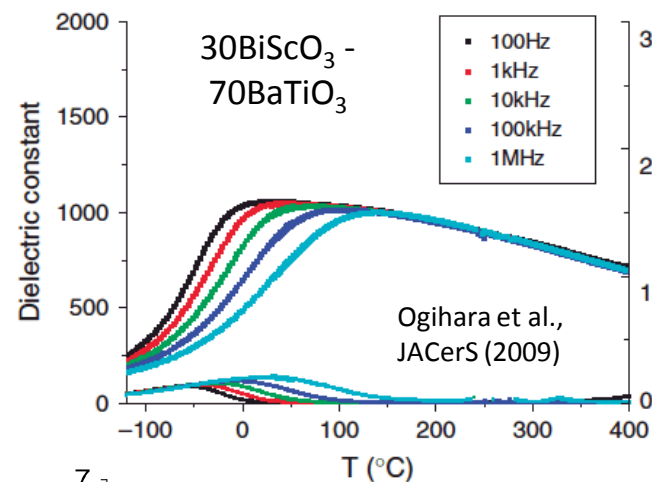
- This work would not have been possible without:
  - Alice Kilgo
  - Bonnie McKenzie
  - Joe Michael
  - Ping Lu
  - Kevin Ring (NM Tech)
  - Yu Hong Jeon (OSU)
  - Adrian Casias
  - Adrian Wagner
  - Mark Rodriguez
  - John Borchardt
  - Greg Lyons
  - Jim Klarkowski



# Capacitor Needs for Grid Storage



# Bi-modified BaTiO<sub>3</sub> Relaxors



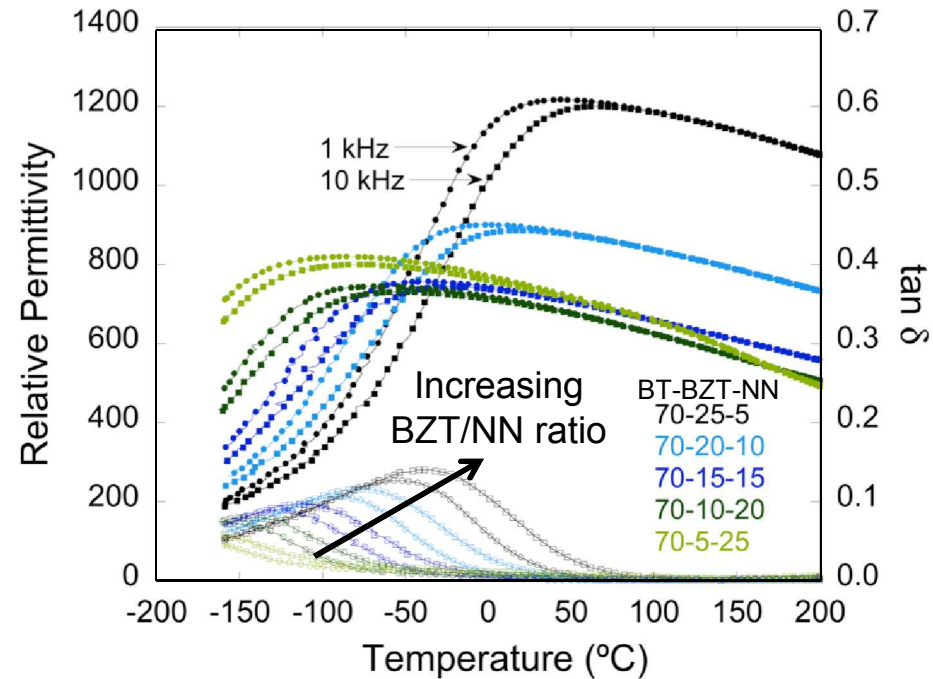
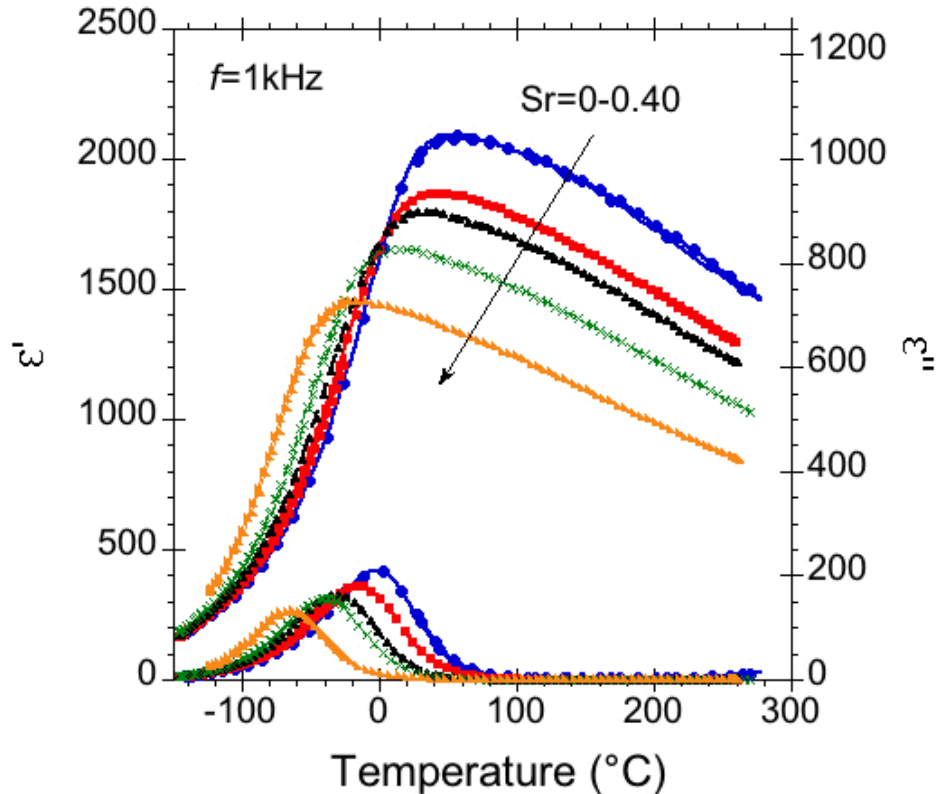
- ‘Weakly-coupled relaxors’

- BaTiO<sub>3</sub> +

- Bi(Zn<sub>0.5</sub>Ti<sub>0.5</sub>)O<sub>3</sub>
- Bi(Mg<sub>0.5</sub>Ti<sub>0.5</sub>)O<sub>3</sub>
- BiScO<sub>3</sub>
- ...

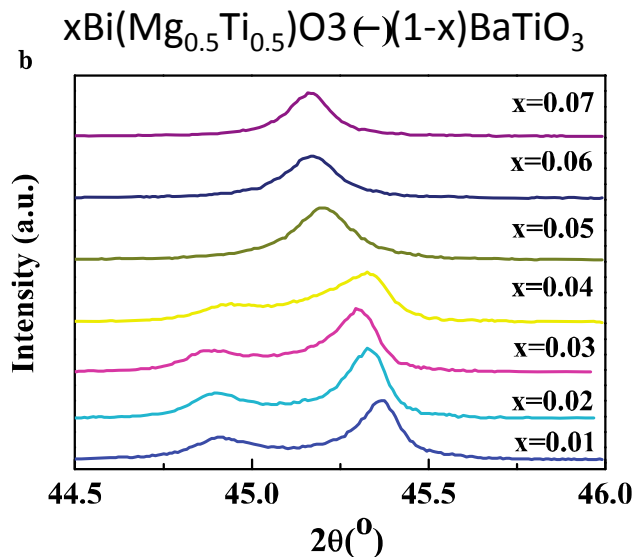
- Voltage stable, moderately-high permittivity above relaxor transition

# BT-BZT: Modifications can Shift $T_{\max}$

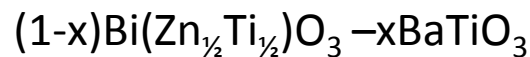
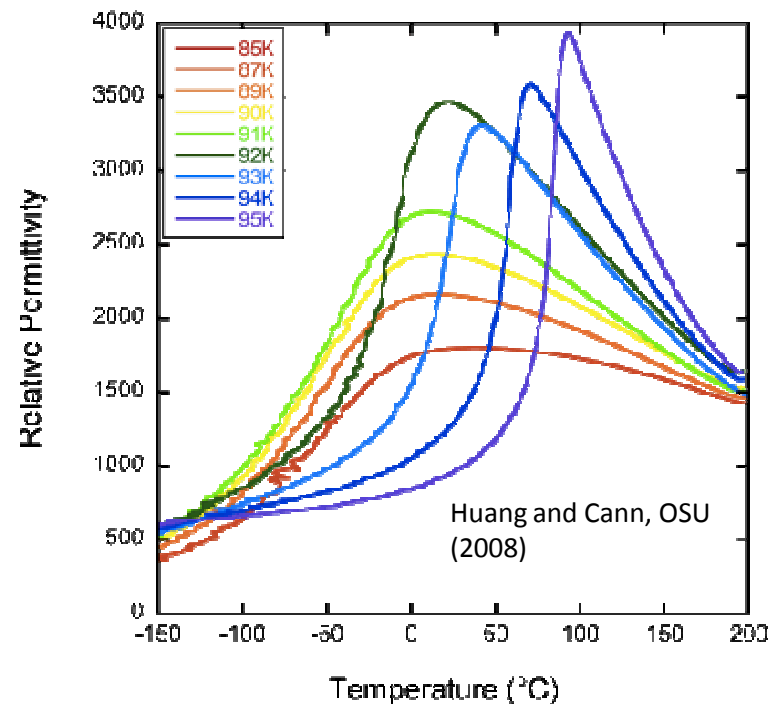
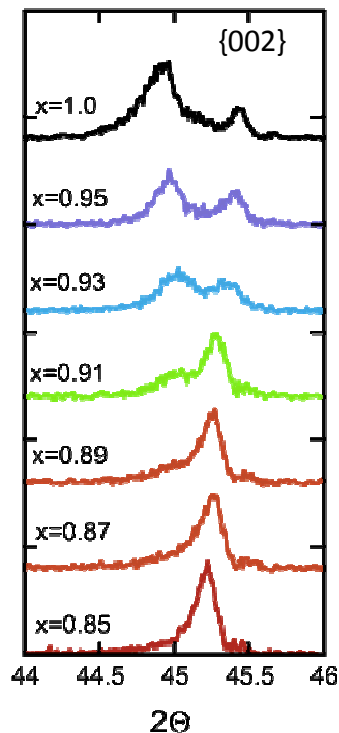
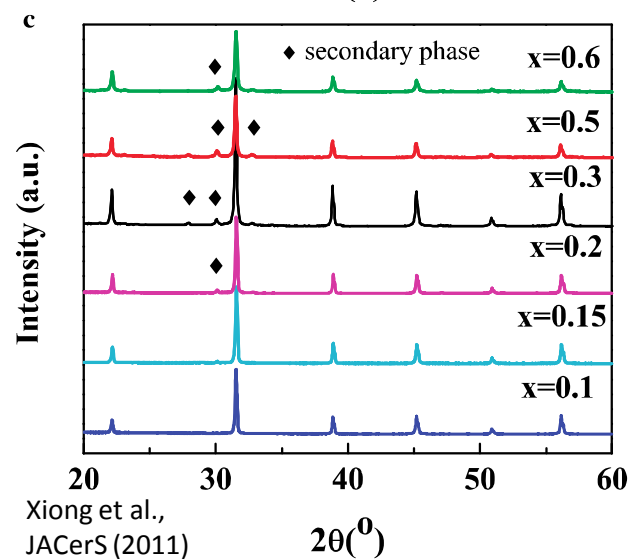


- $\text{NaNbO}_3$ ,  $\text{SrTiO}_3$ ,  $\text{BaZrO}_3$ ,  $\text{La}_{\text{Bi}}^x$ , etc. shift  $T_{\max}$  down
- $\text{BiScO}_3$ ,  $\text{PbTiO}_3$  and others shift  $T_{\max}$  up

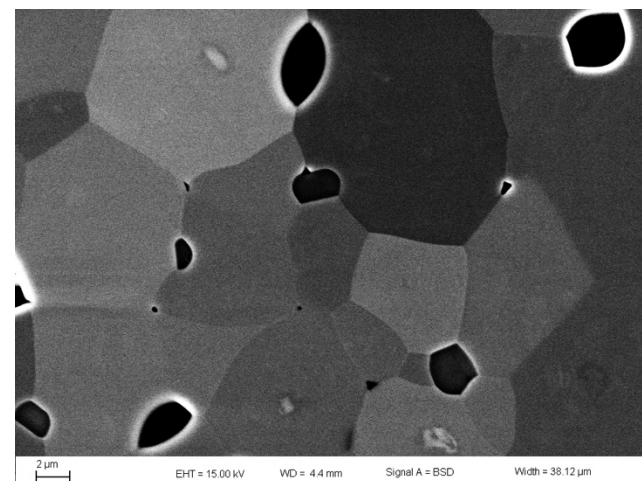
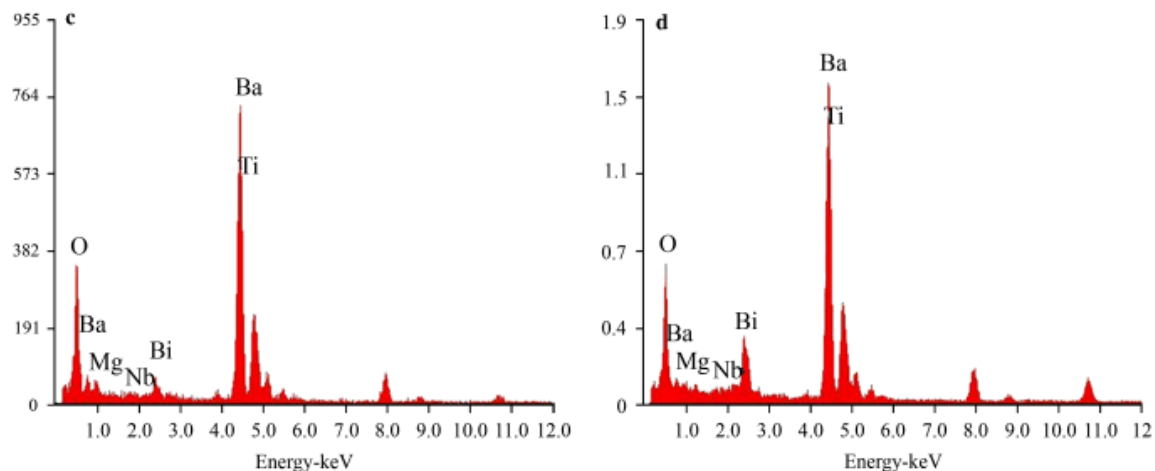
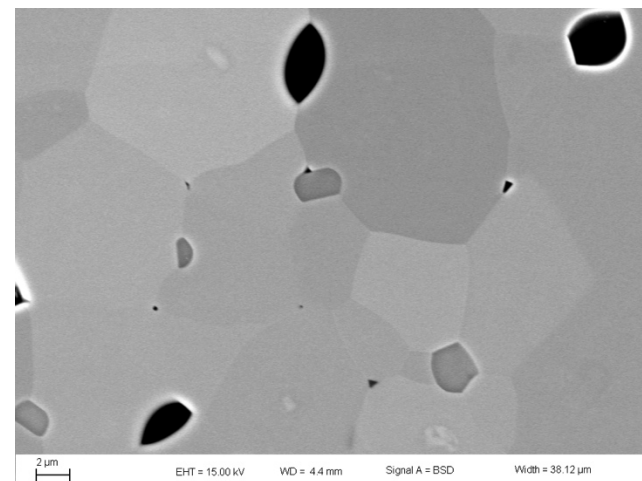
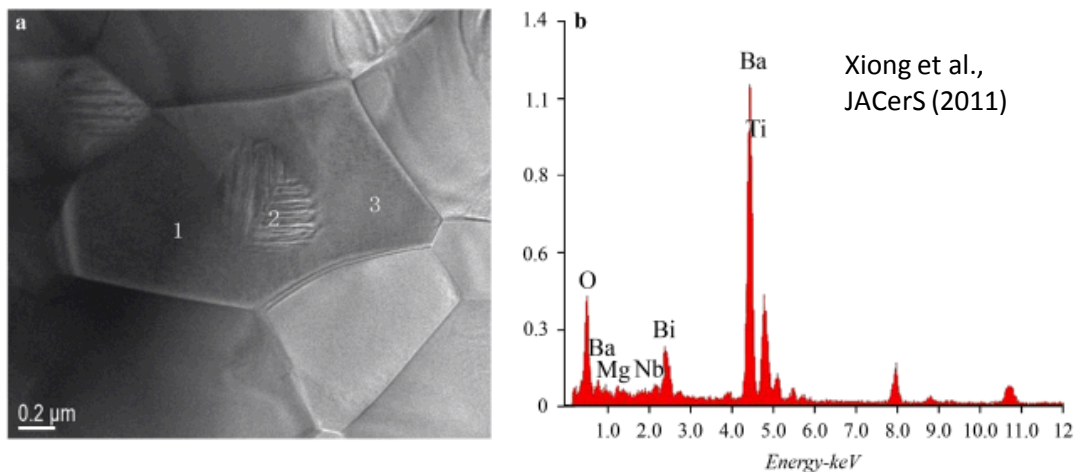
# Diffraction Studies are Limited



- Pure  $\text{Bi}(\text{Zn}_{0.5}\text{Ti}_{0.5})\text{O}_3$  and  $\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$  end members unstable; additional phases observed for large substitutions
- Unusual behaviors suggest complexity...

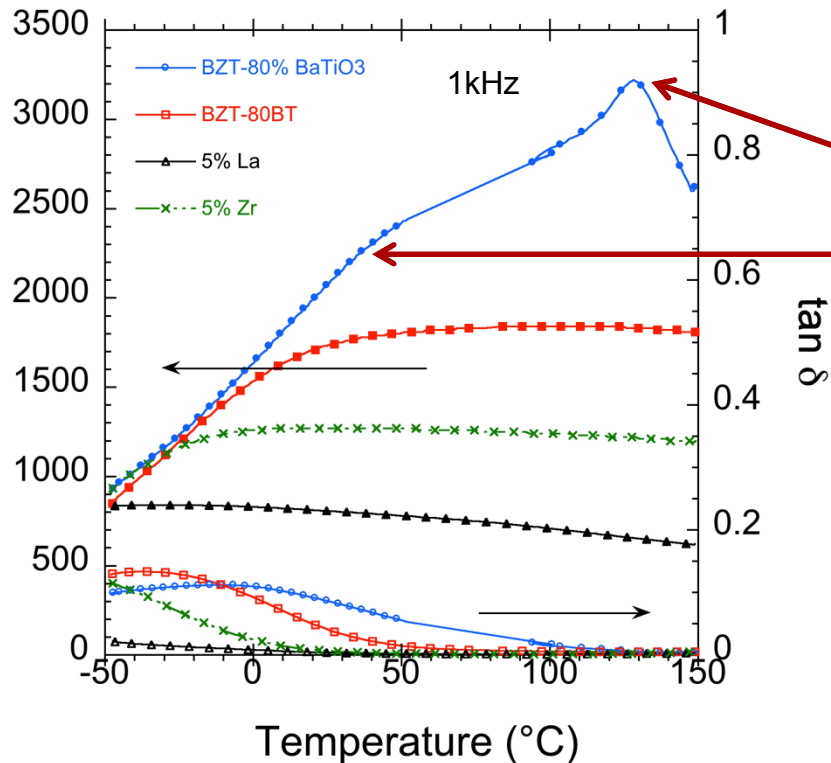


# BT-BZT: Modifications can Shift $T_{\max}$

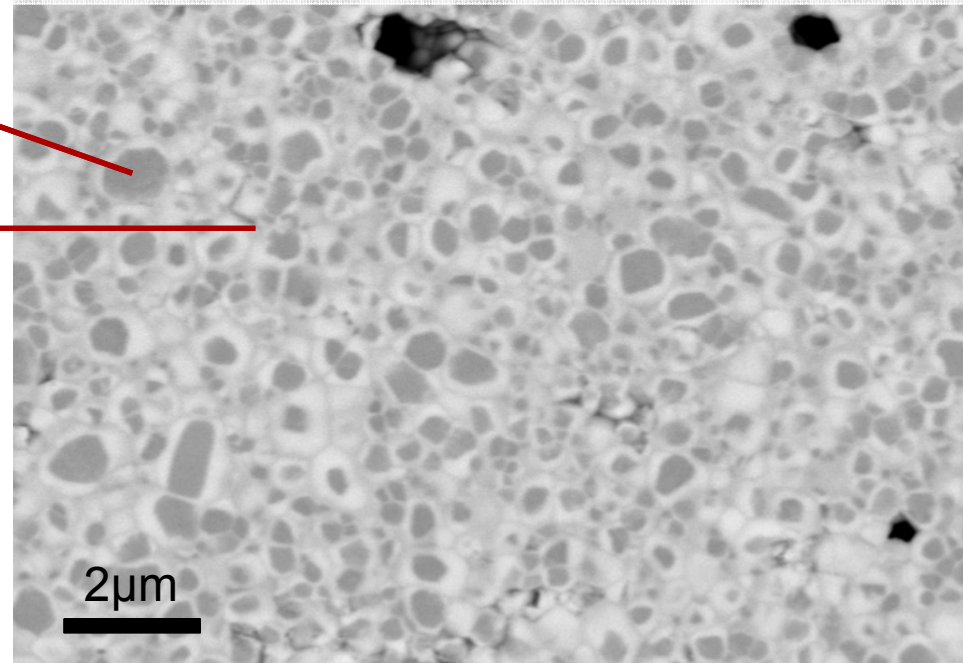


- Reminder: 'single phase by XRD' != homogeneous

# BT-BZT: Modifications can Shift $T_{\max}$



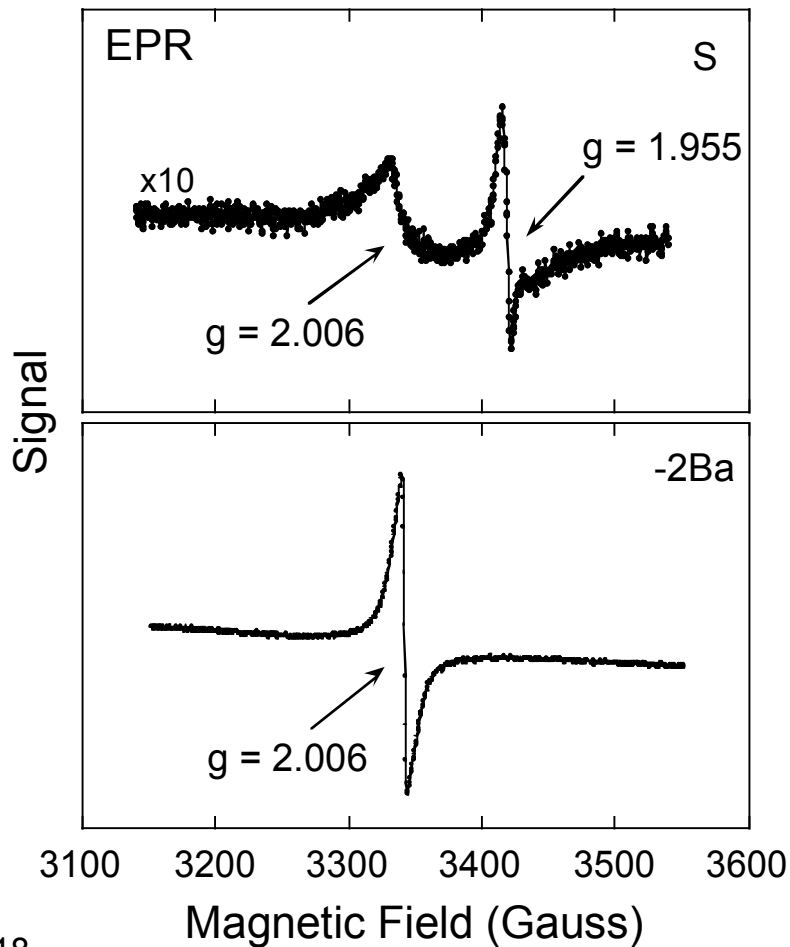
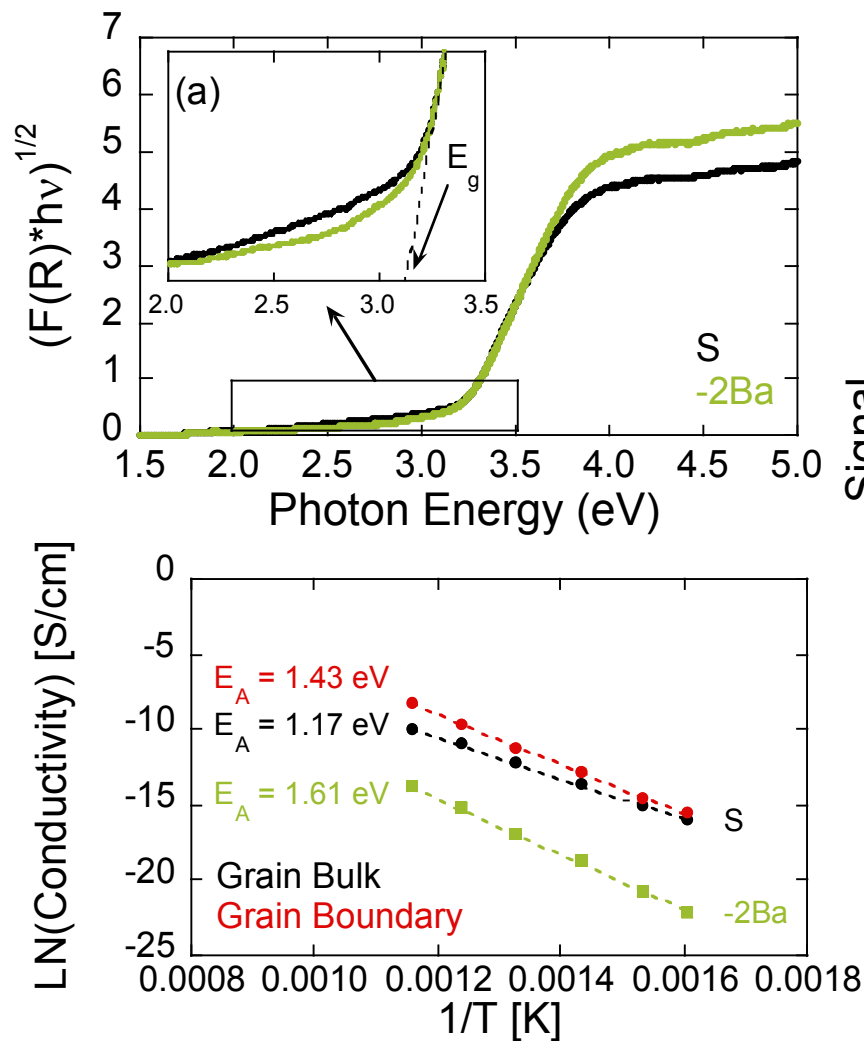
Intentionally fabricated BaTiO<sub>3</sub> core, Bi-rich shell



Core exhibits  $T_C \sim 125^{\circ}\text{C}$   
Shell exhibits relaxor behavior

- Reminder: 'single phase by XRD' != homogeneous

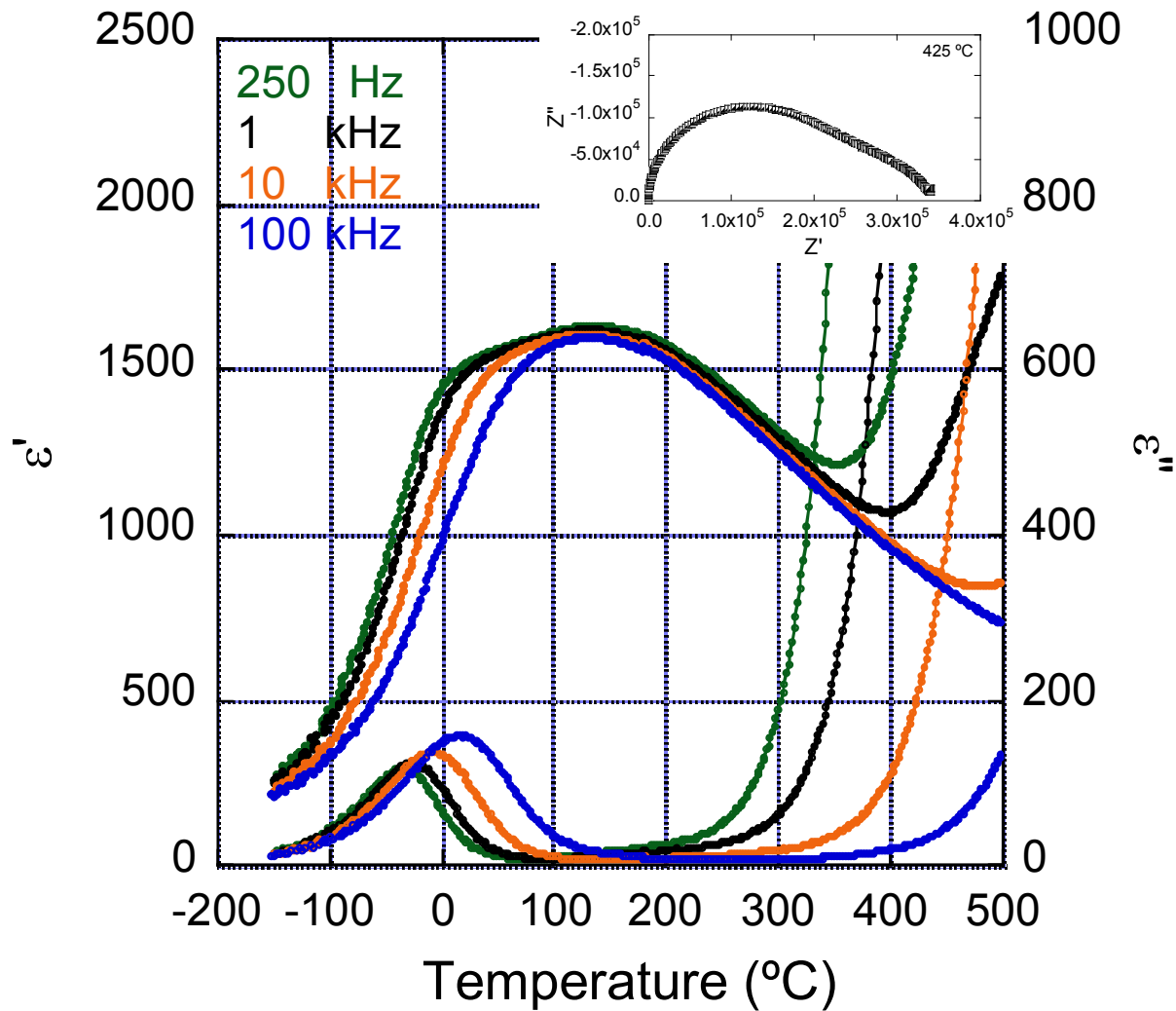
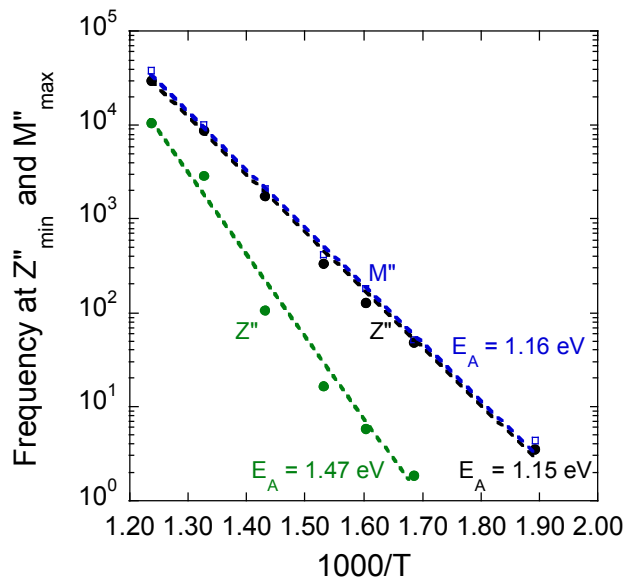
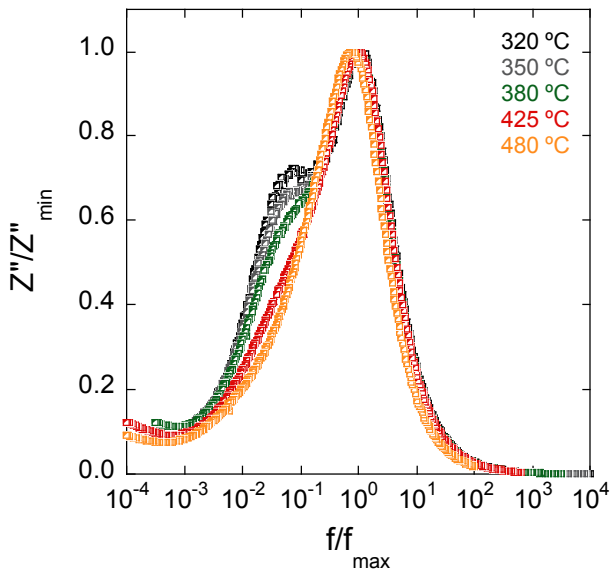
# Defects: Optical & Electrical Info



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

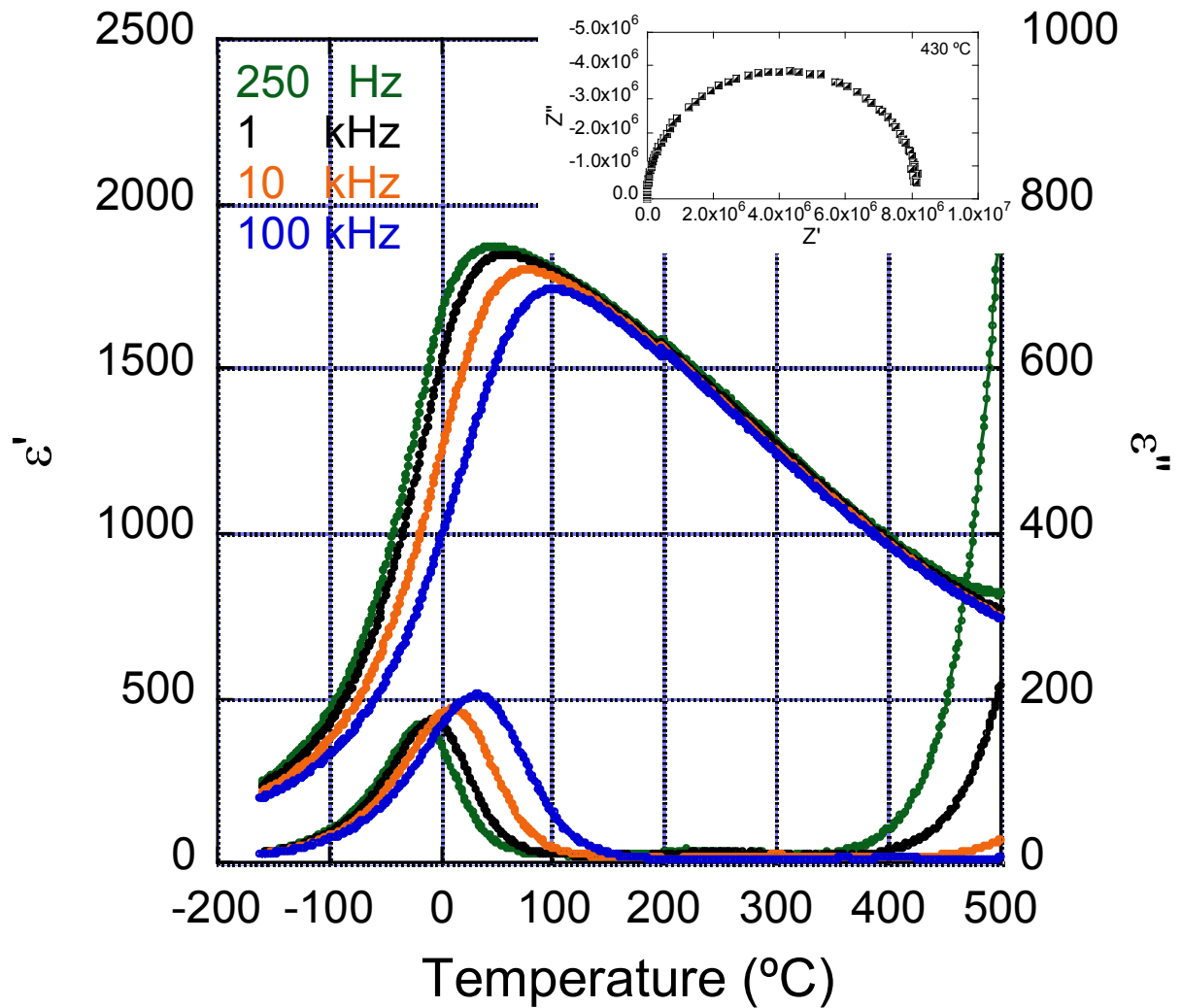
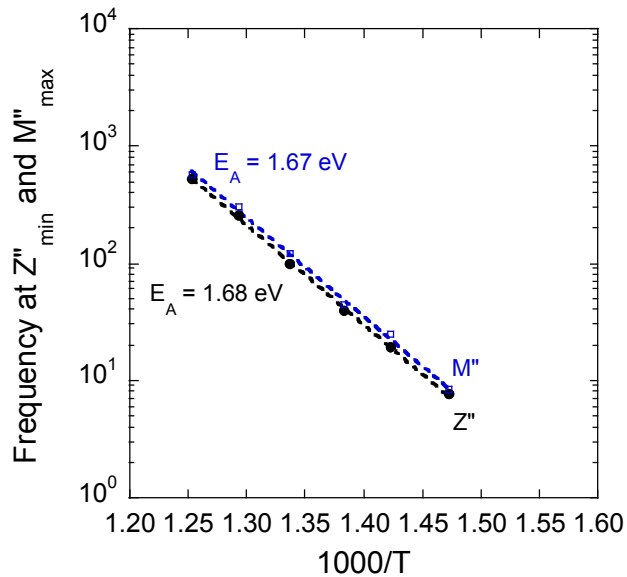
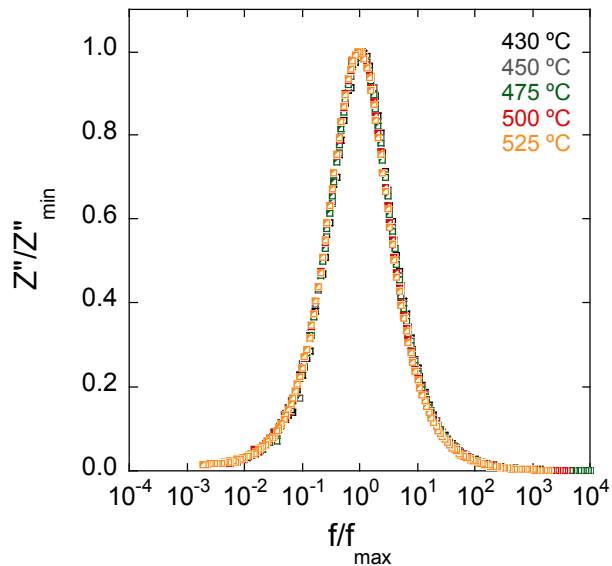
- Defect studies suggest  $V_{Ba}'' - V_O^{\bullet\bullet}$  pairs are strong carrier traps

# Nominally Stoichiometric, Acceptor



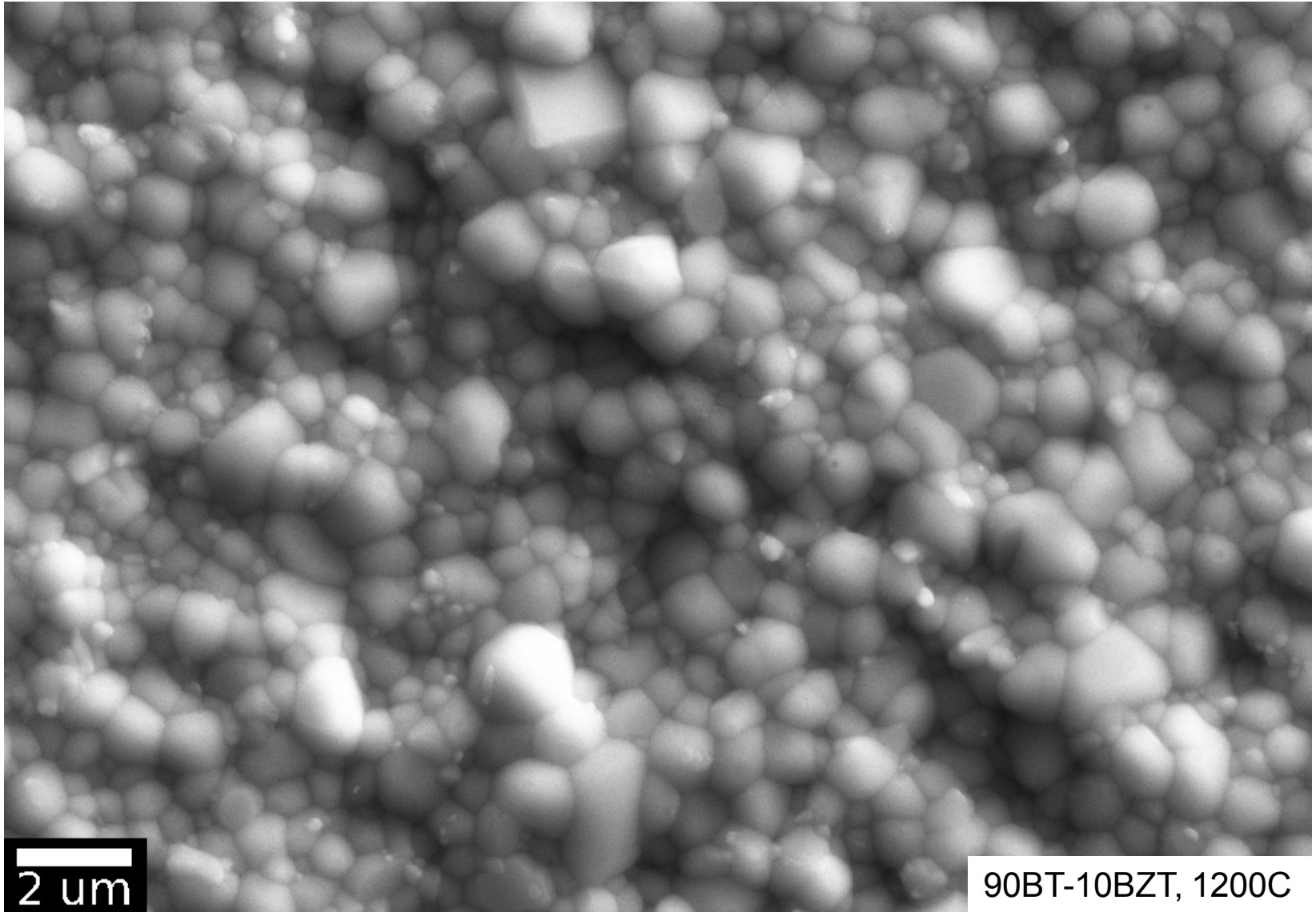
- (Nominally) stoichiometric and acceptor-doped samples are 'electrically heterogeneous'

# Donor-Doped

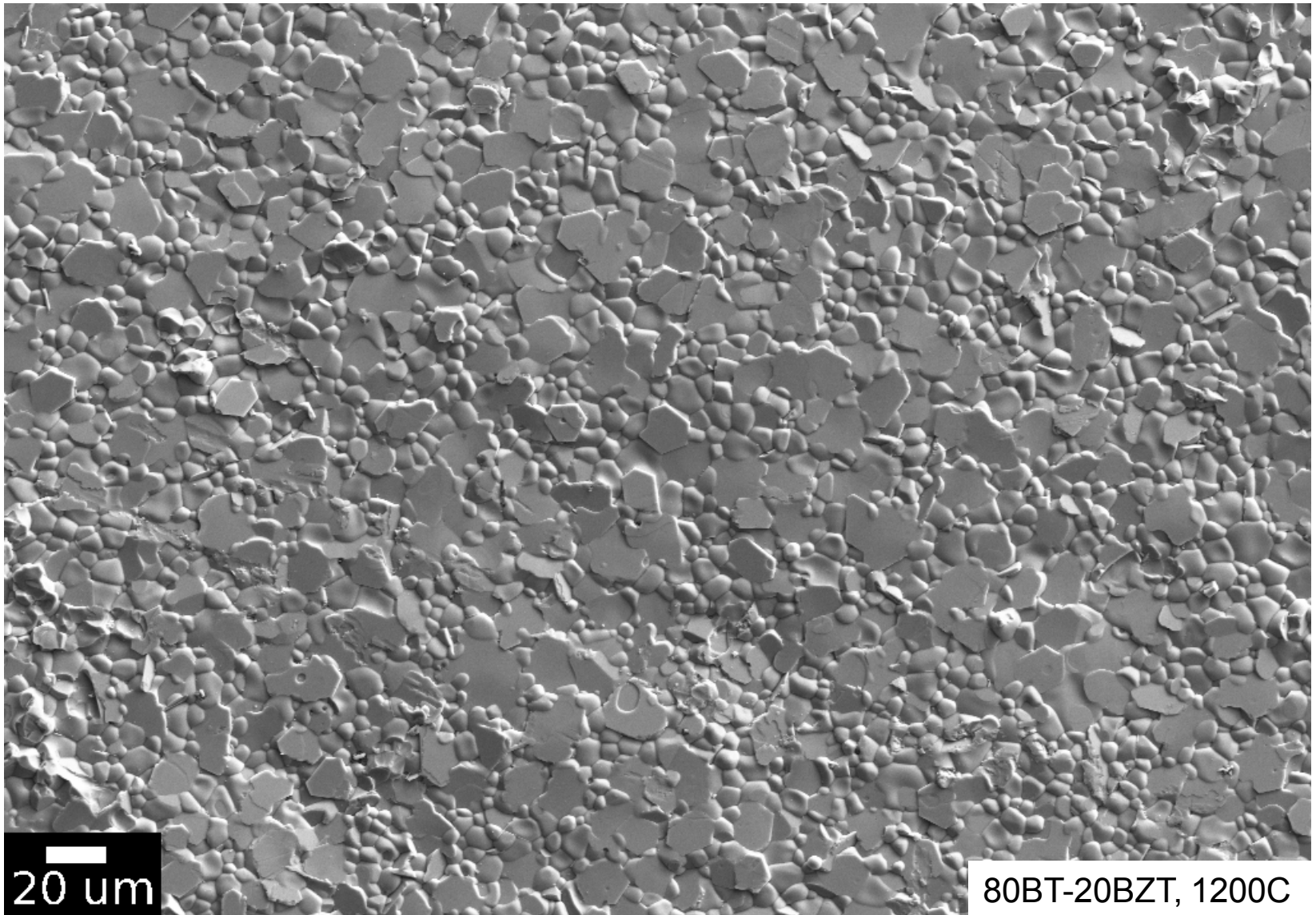


■ Donor-doped samples are 'electrically homogeneous'

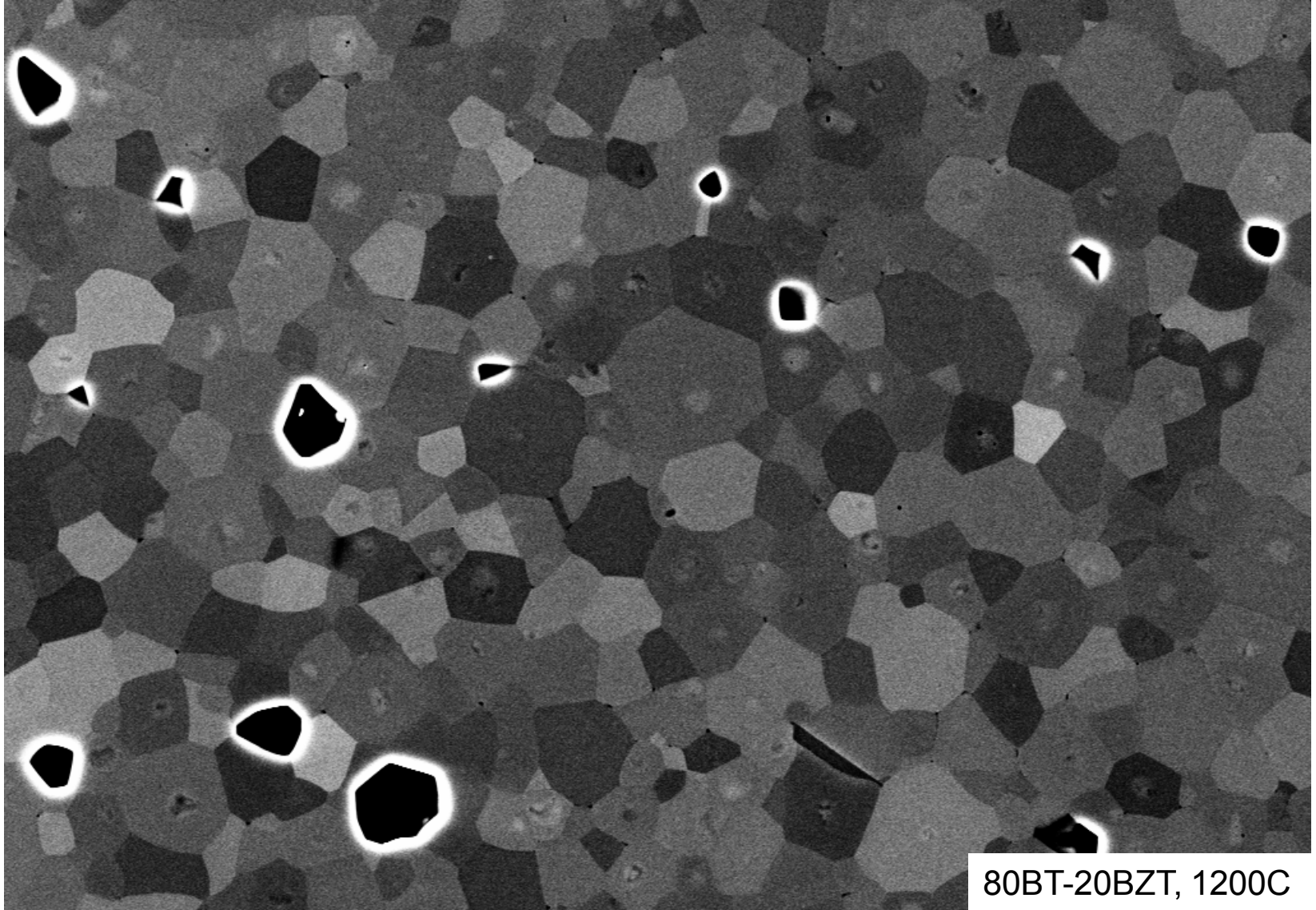
# Typical Microstructures



# Typical Microstructures



# Typical Microstructures

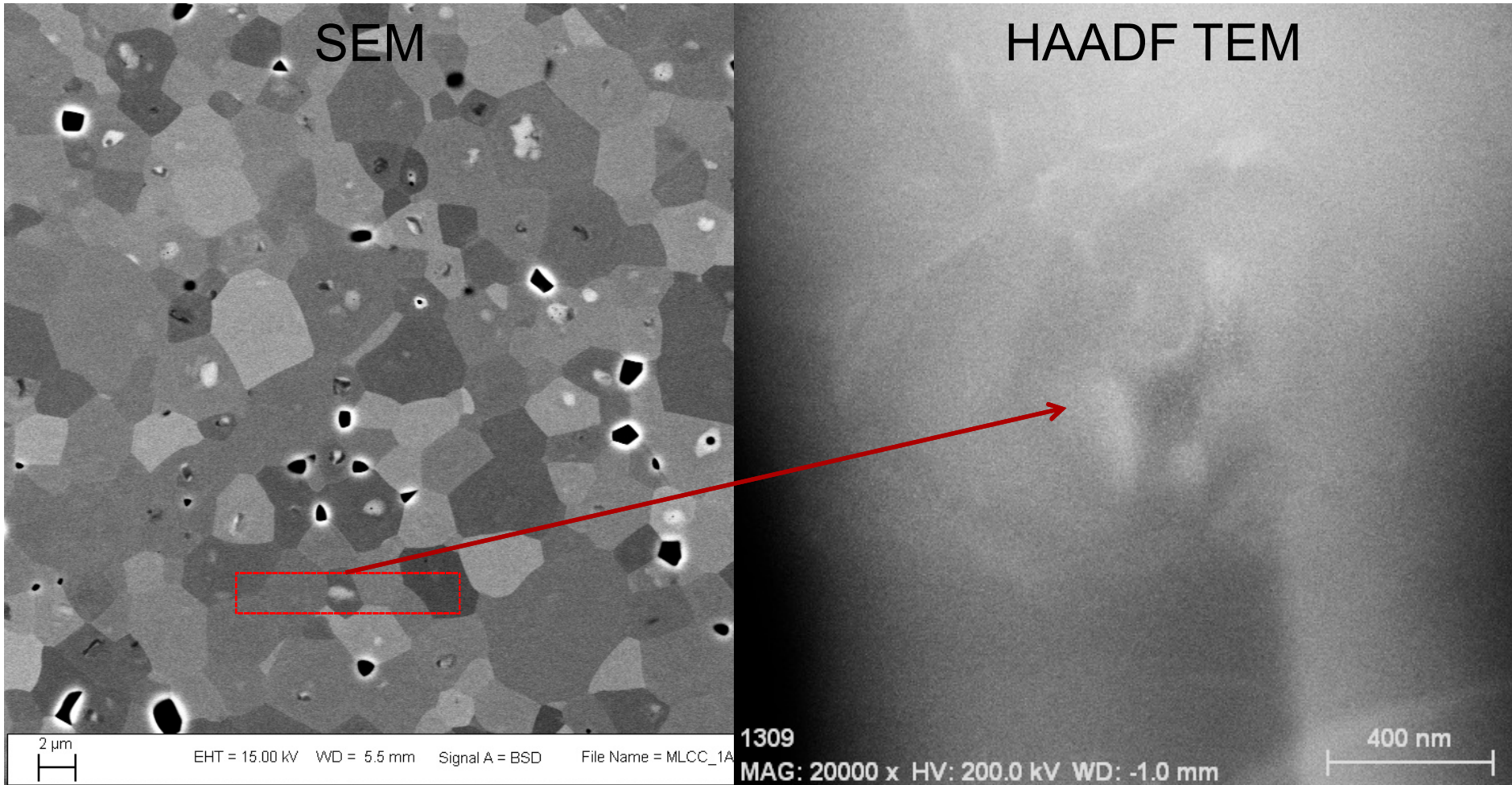


80BT-20BZT, 1200C

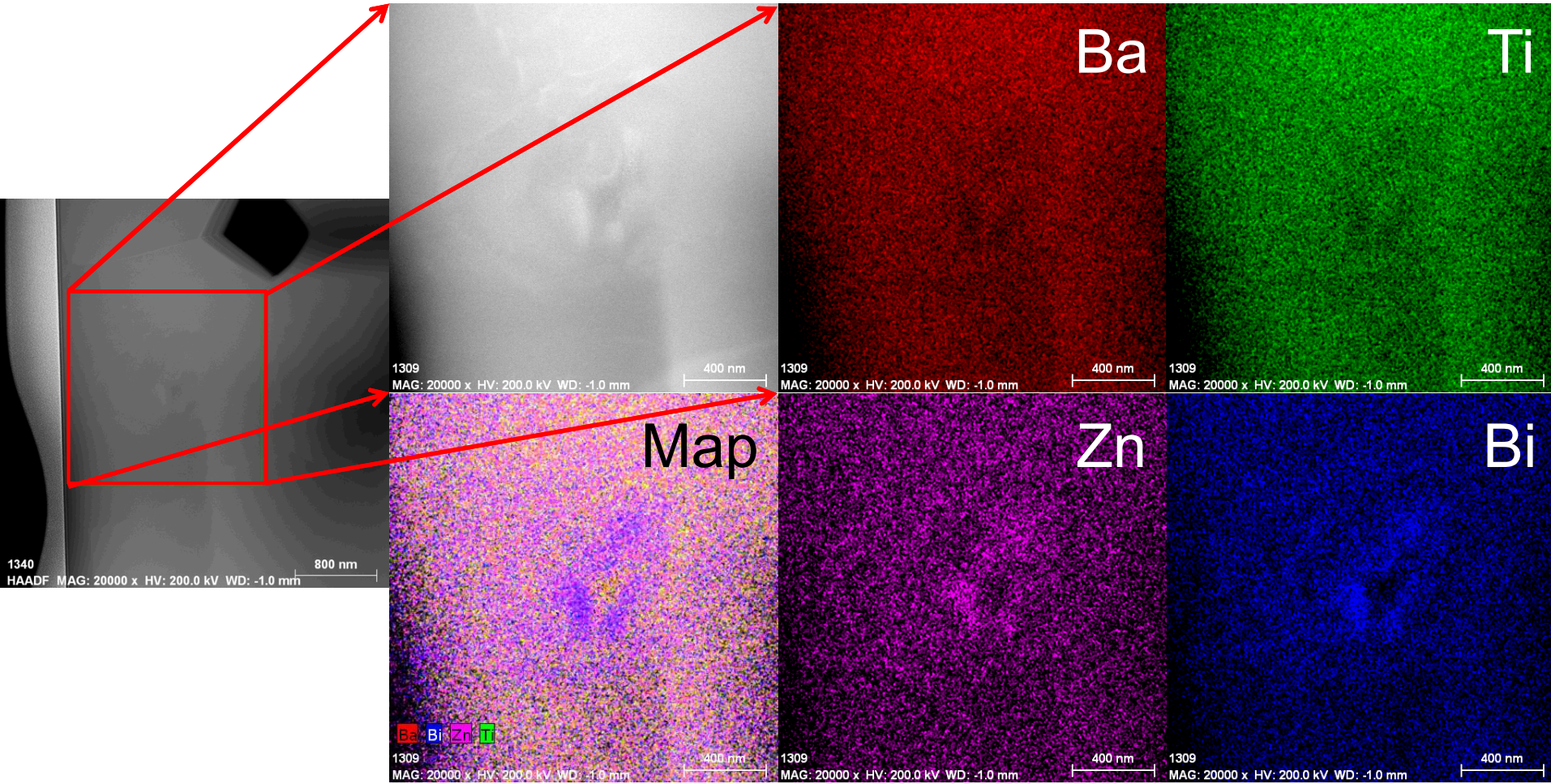
2  $\mu$ m

EHT = 15.00 kV WD = 3.8 mm Signal A = BSD File Name = BZT-80BT\_43.tif

# Compositional Variation



# Bi and Zn Variation



# Summary

- Electrical response(s) of weakly-coupled relaxor systems tied to multi-scale chemical heterogeneities
- Complex microscale chemical distributions appear to be (somewhat) independent of relaxor behavior, but likely contribute strongly to high-field electrical behavior
- Reminder: no single view (or characterization technique) provides the complete picture!