

Minimizing Voltage Tuning for Enhanced High Field Capacitance

Geoff L. Brennecka,¹ Harlan J. Brown-Shaklee,¹
Natthaphon Raengthon,² David P. Cann,²
David I. Shahin,^{1,3} Ryan P. Wilkerson,^{1,3} Kelsey E. Meyer,^{1,4}
and Yu Hong Jeon^{1,2}

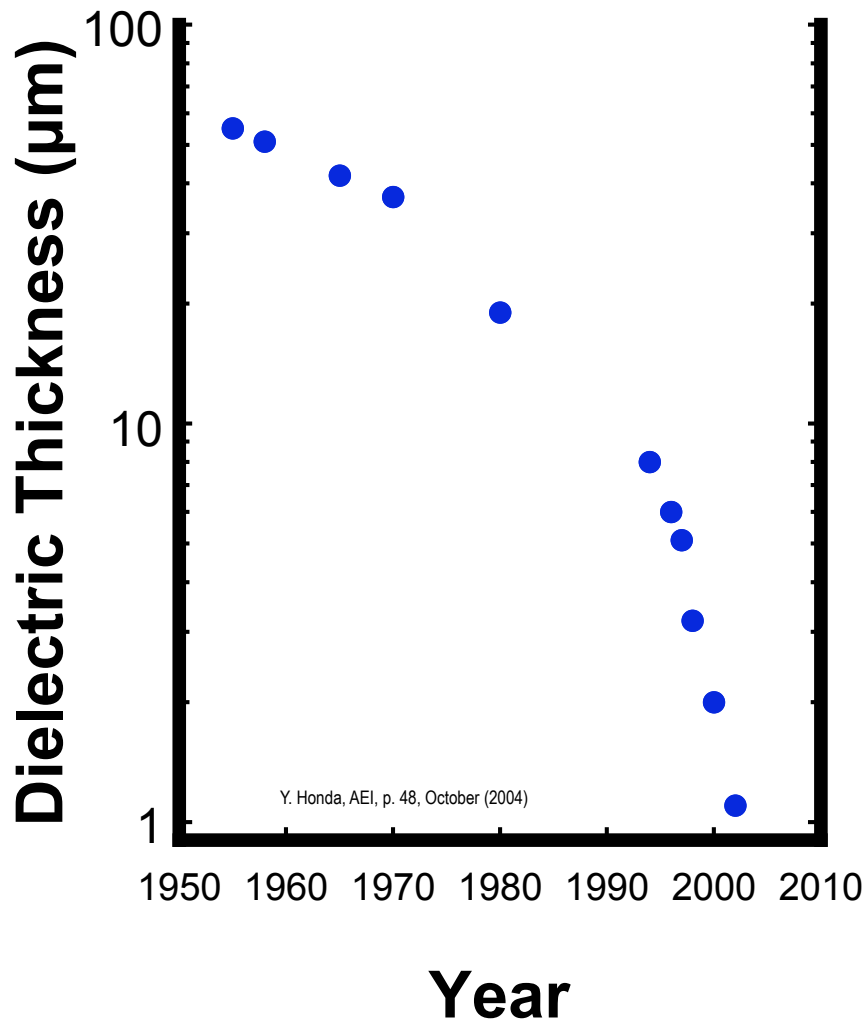
- 1) Sandia National Laboratories, Albuquerque, NM
- 2) Oregon State University, Corvallis, OR
- 3) Missouri University of Science and Technology, Rolla, MO
- 4) New Mexico Institute of Mining and Technology, Socorro, NM

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

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

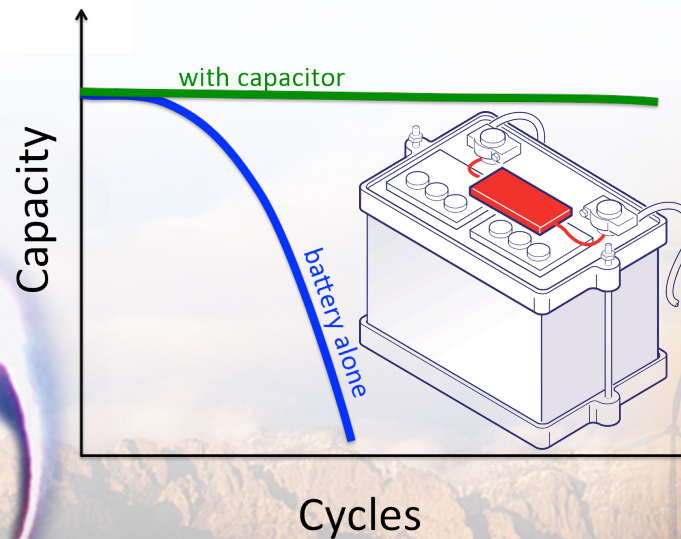
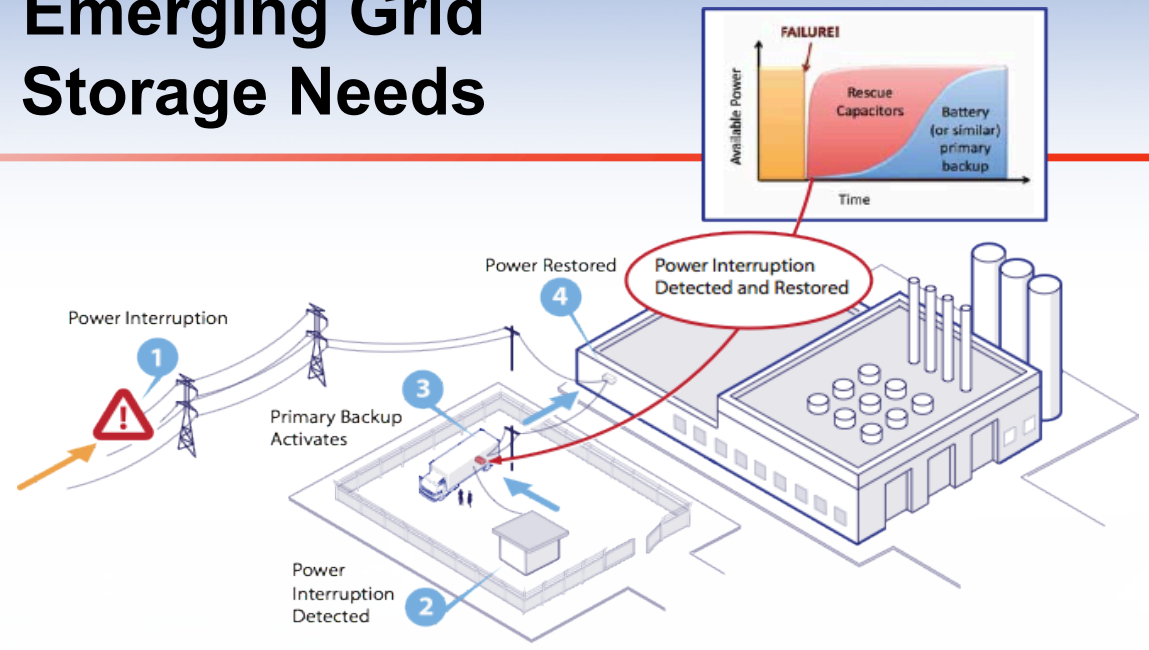
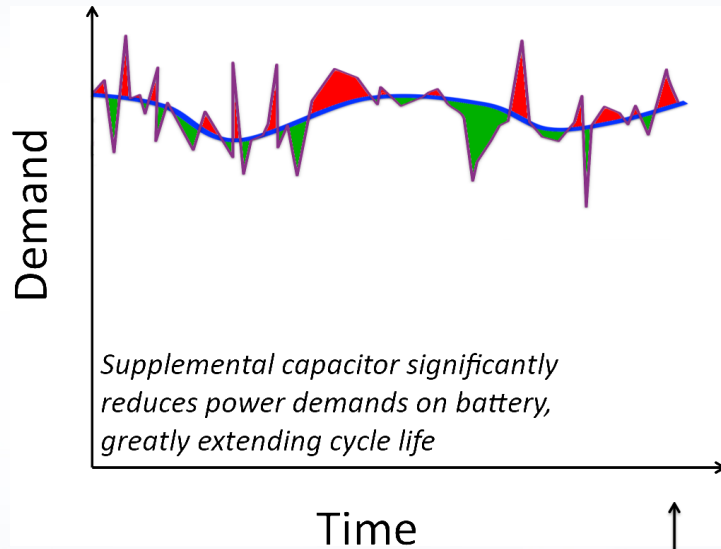


High Field Operation

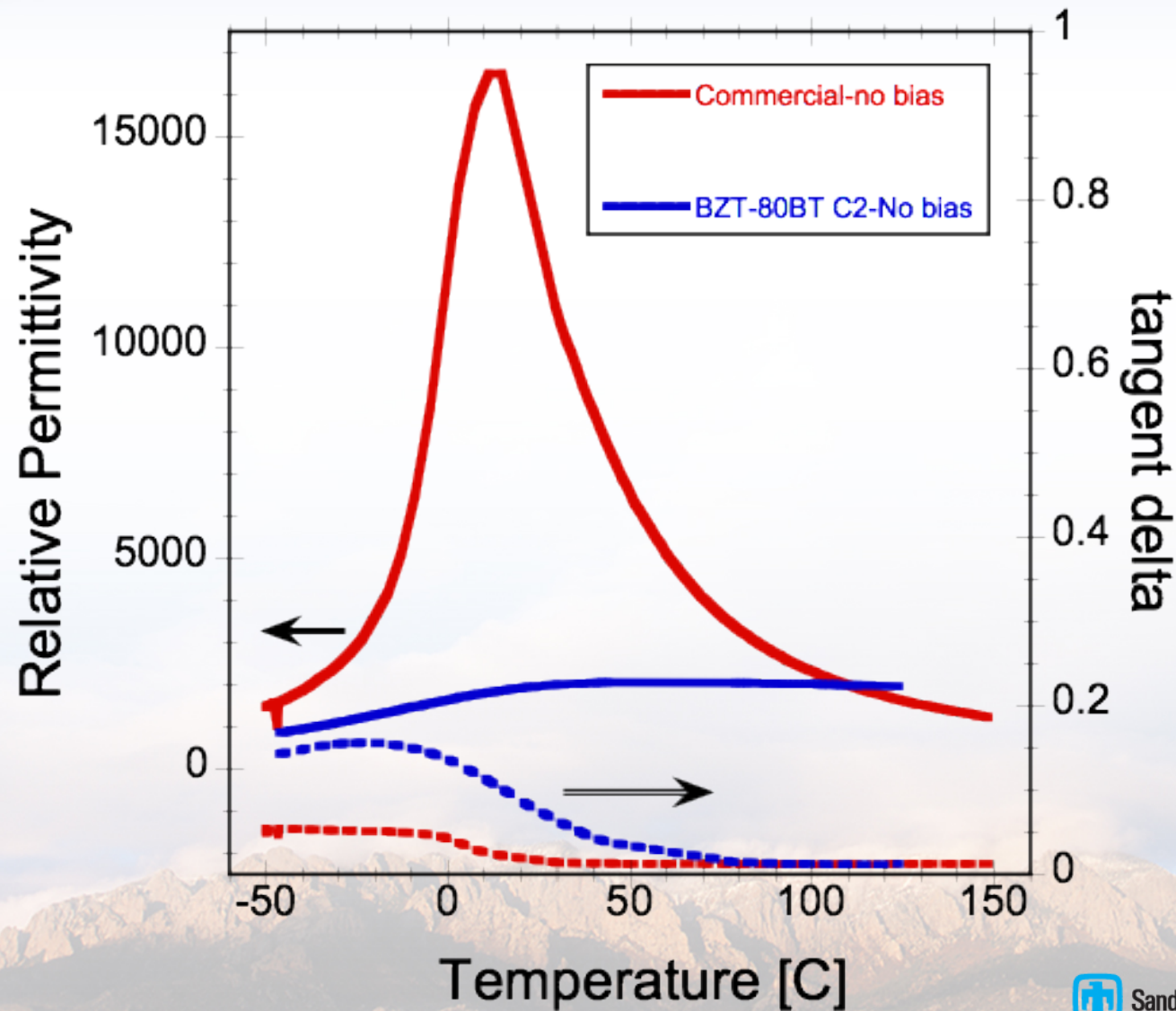


- Thinner layers means higher operating fields
- Many applications require high energy and/or high capacitance under dc bias (blocking caps, pulse discharge, power electronics, etc.)
- Reliable operation under bias (especially at elevated temperatures) requires precise defect control

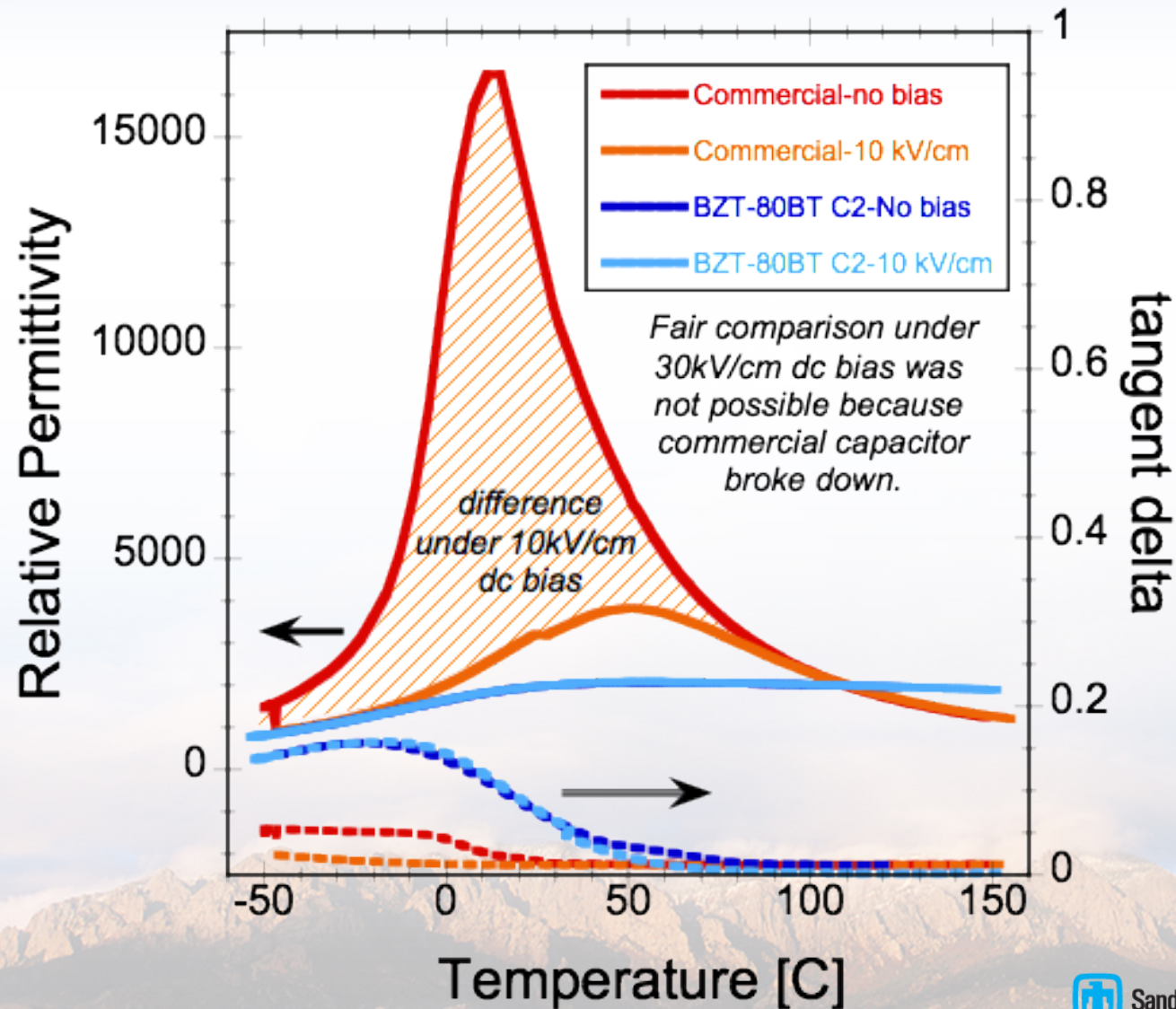
Emerging Grid Storage Needs



Tuning Under Bias

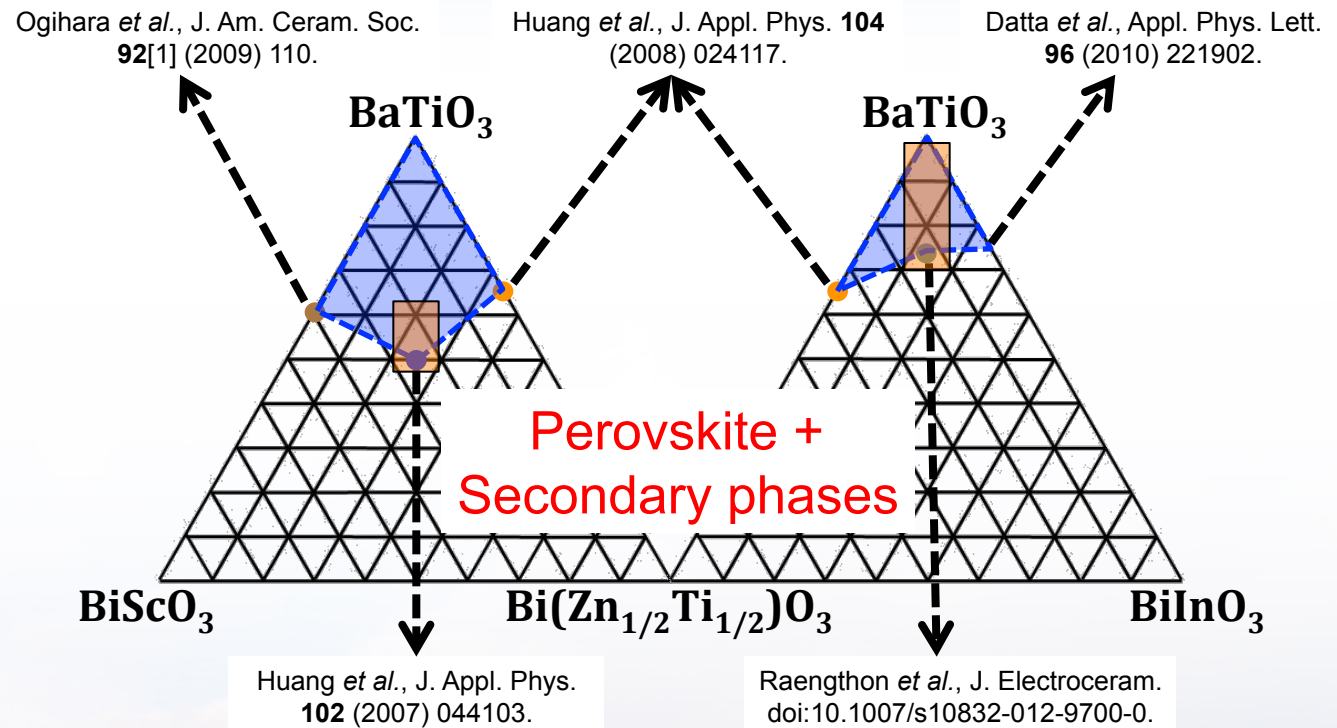


Tuning Under Bias



Bi(M)O₃ – BaTiO₃ Solid Solutions

(M)
 Sc
 In
 Fe
 Mg_{0.5}Ti_{0.5}
 Mg_{0.5}Zr_{0.5}
 Zn_{0.5}Ti_{0.5}
 Zn_{0.5}Zr_{0.5}
 Ni_{0.5}Ti_{0.5}
 Mg_{0.75}W_{0.25}
 ⋮

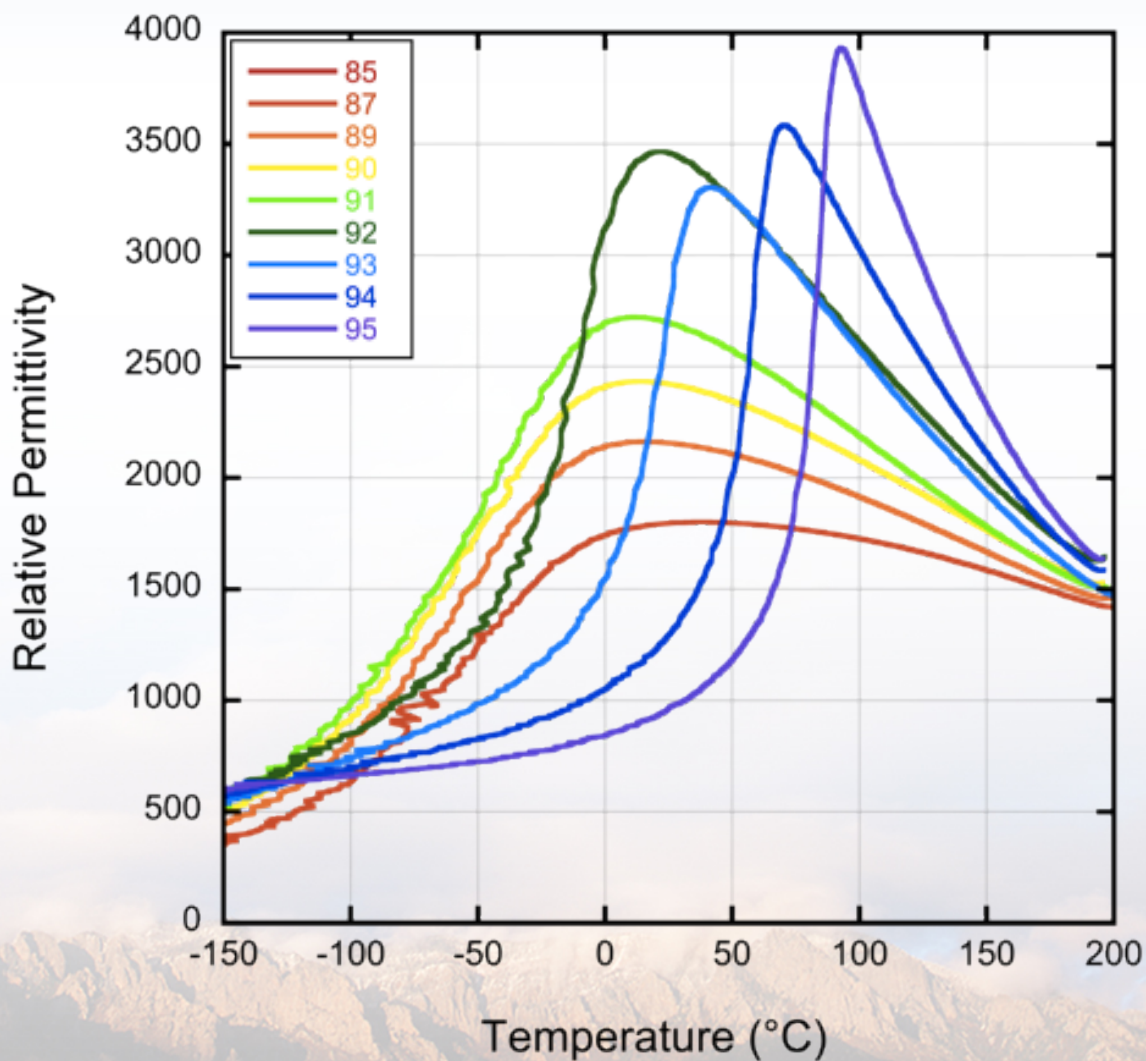
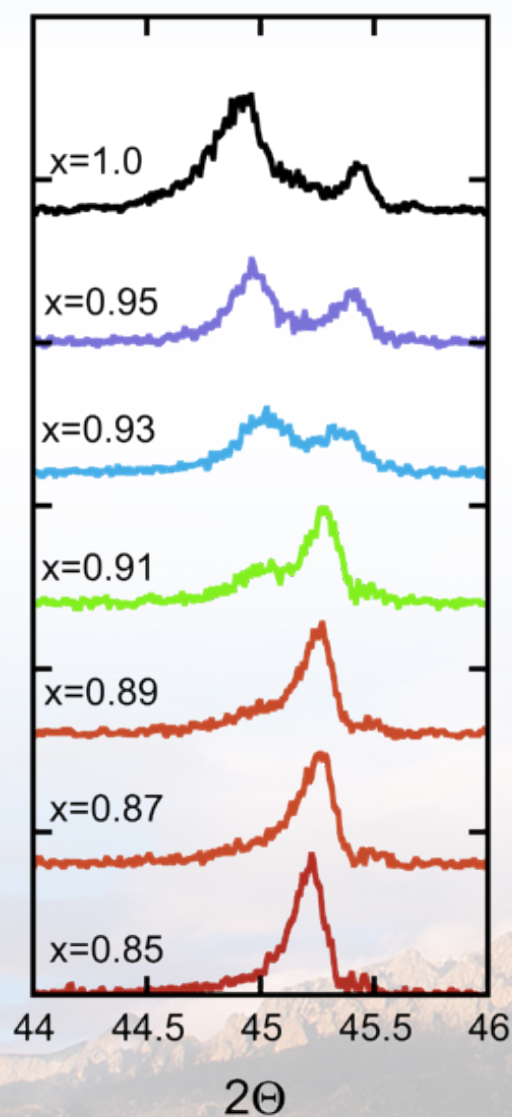


Eitel and Randall performed pioneering work on Bi-based solid solutions with PbTiO₃ for high-T_C piezoelectrics following simulations from Davies *et al.*

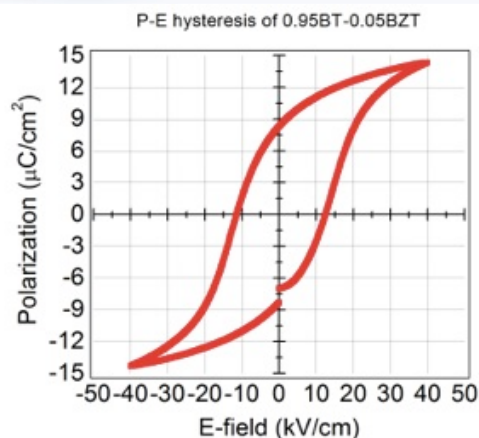
Also literature on Bi(Zn_{0.5}Ti_{0.5})O₃ as end member with NaNbO₃, Bi(Na,K)TiO₃, etc.

Majority of work on these systems has focused on maximizing piezoelectric response

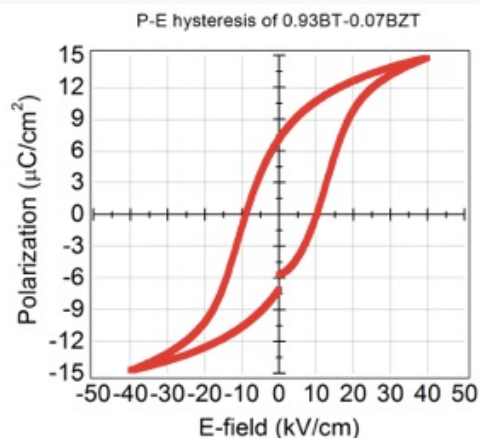
$(1-x)\text{Bi}(\text{Zn}_{0.5}\text{Ti}_{0.5})\text{O}_3 - x\text{BaTiO}_3$



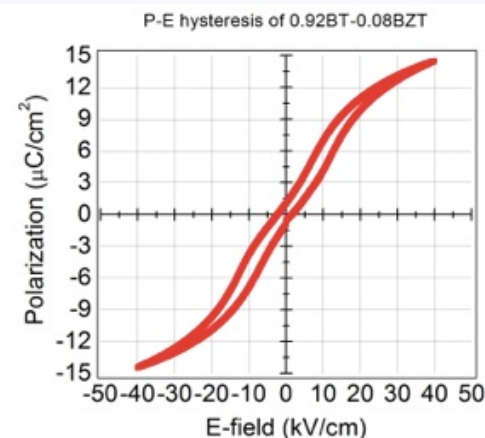
$(1-x)\text{Bi}(\text{Zn}_{0.5}\text{Ti}_{0.5})\text{O}_3 - x\text{BaTiO}_3$



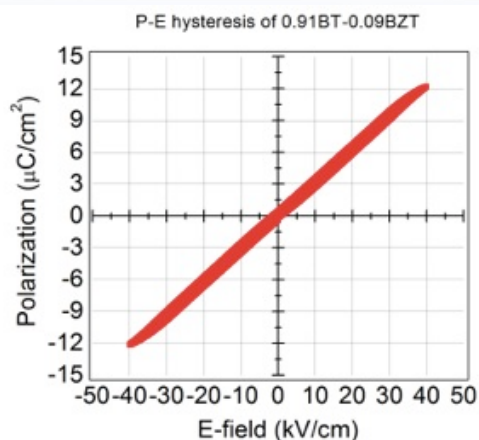
$x = 0.95$



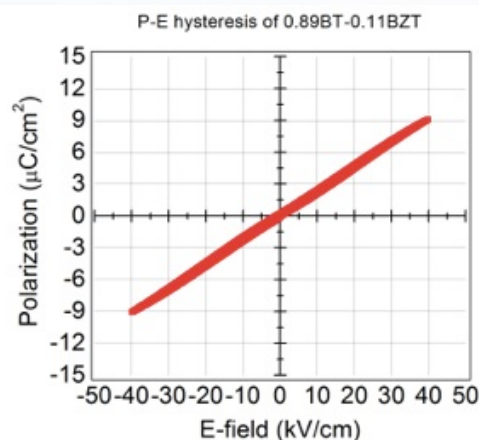
$x = 0.93$



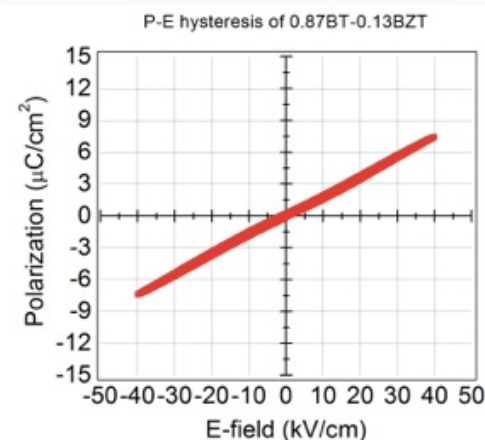
$x = 0.92$



$x = 0.91$



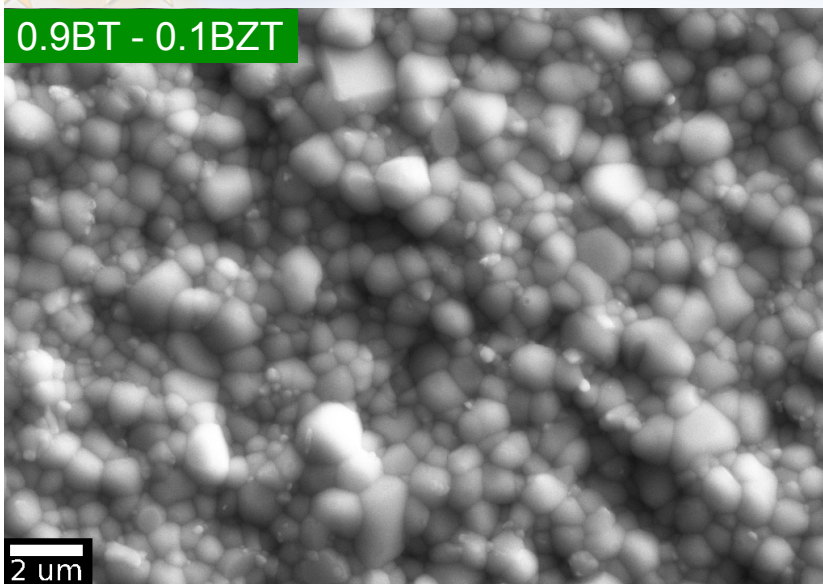
$x = 0.89$



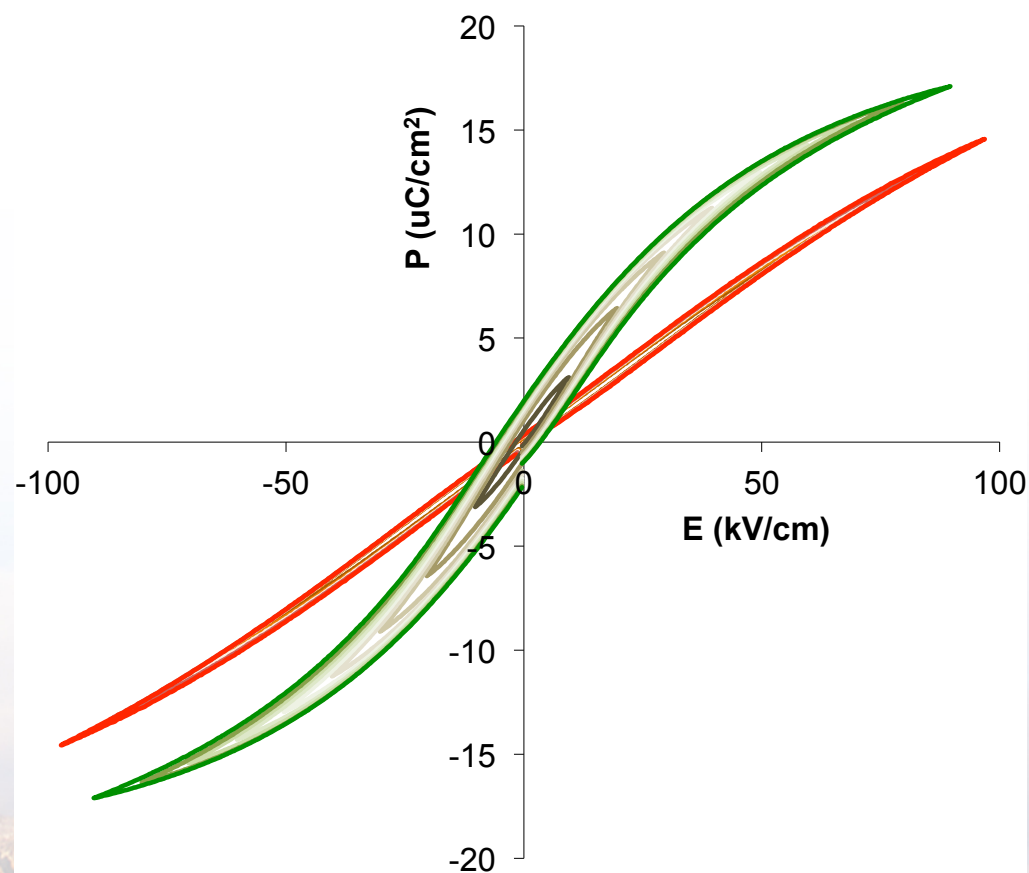
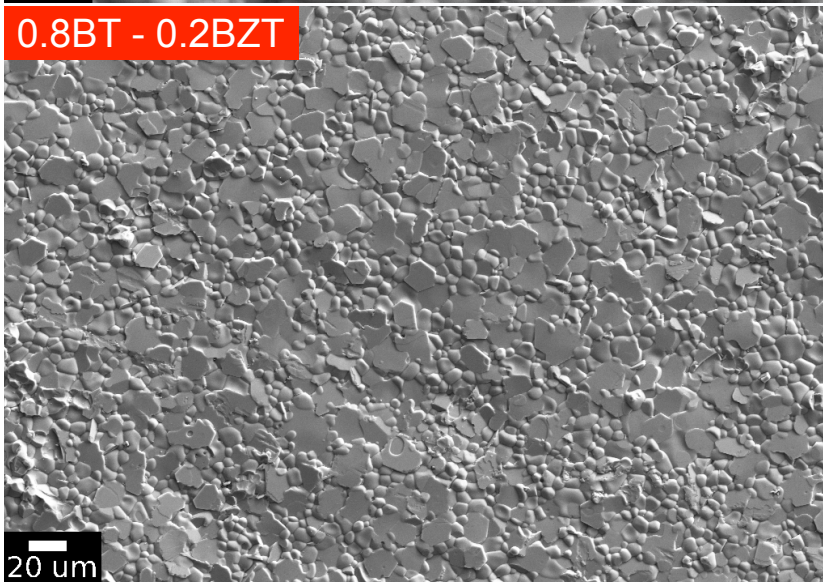
$x = 0.87$

$(1-x)\text{Bi}(\text{Zn}_{0.5}\text{Ti}_{0.5})\text{O}_3 - x\text{BaTiO}_3$

0.9BT - 0.1BZT

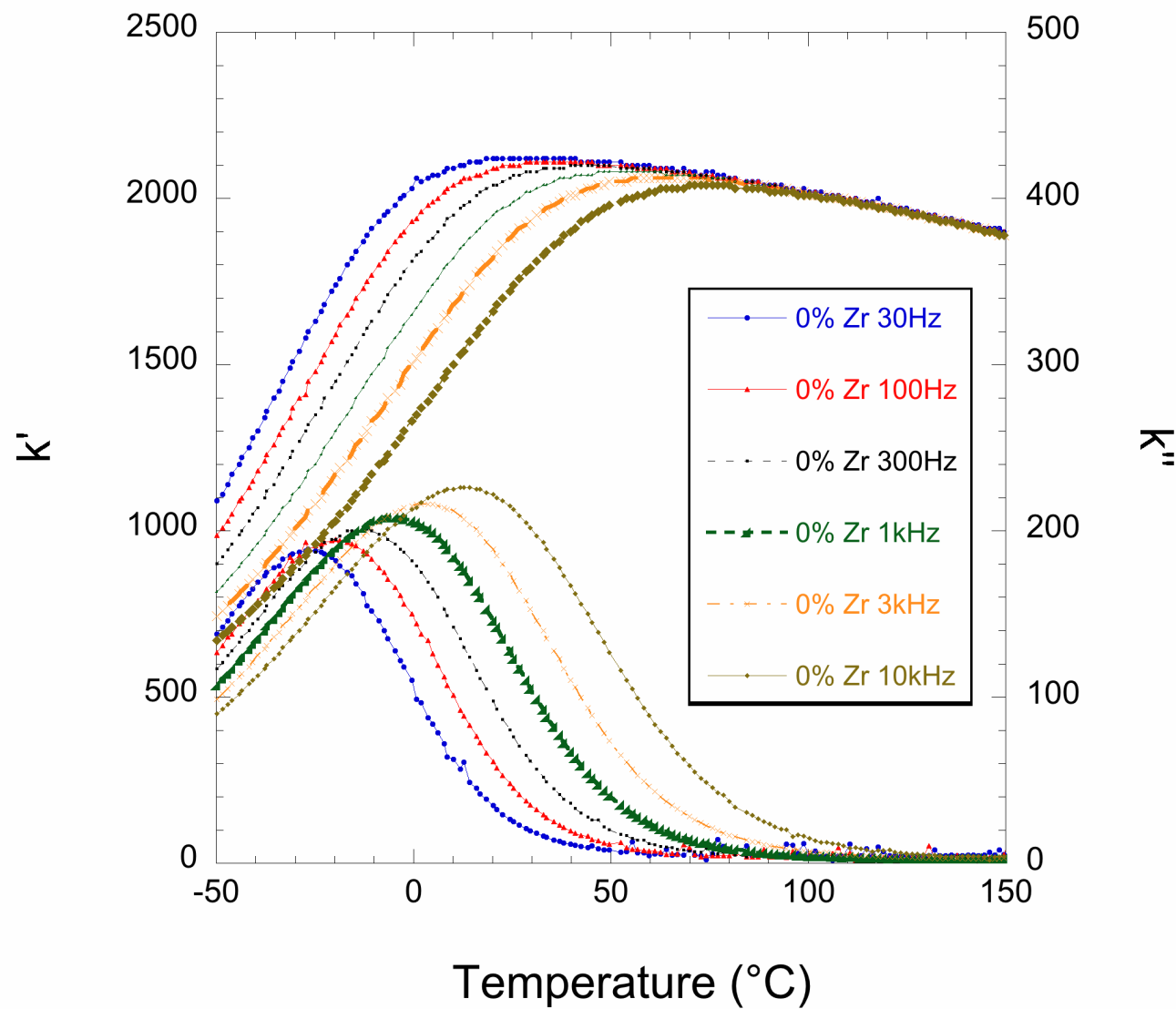


0.8BT - 0.2BZT

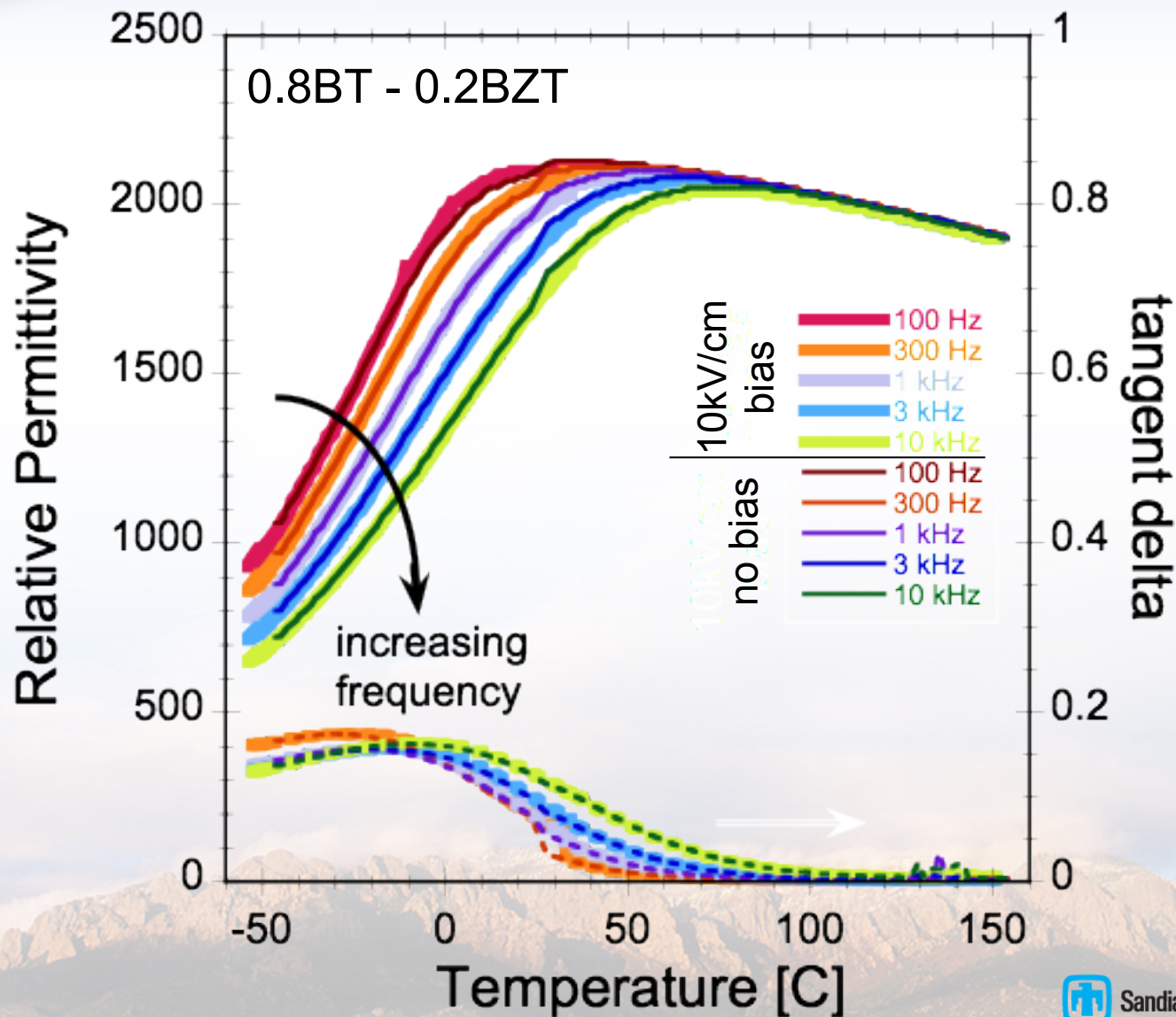


Sandia National Laboratories

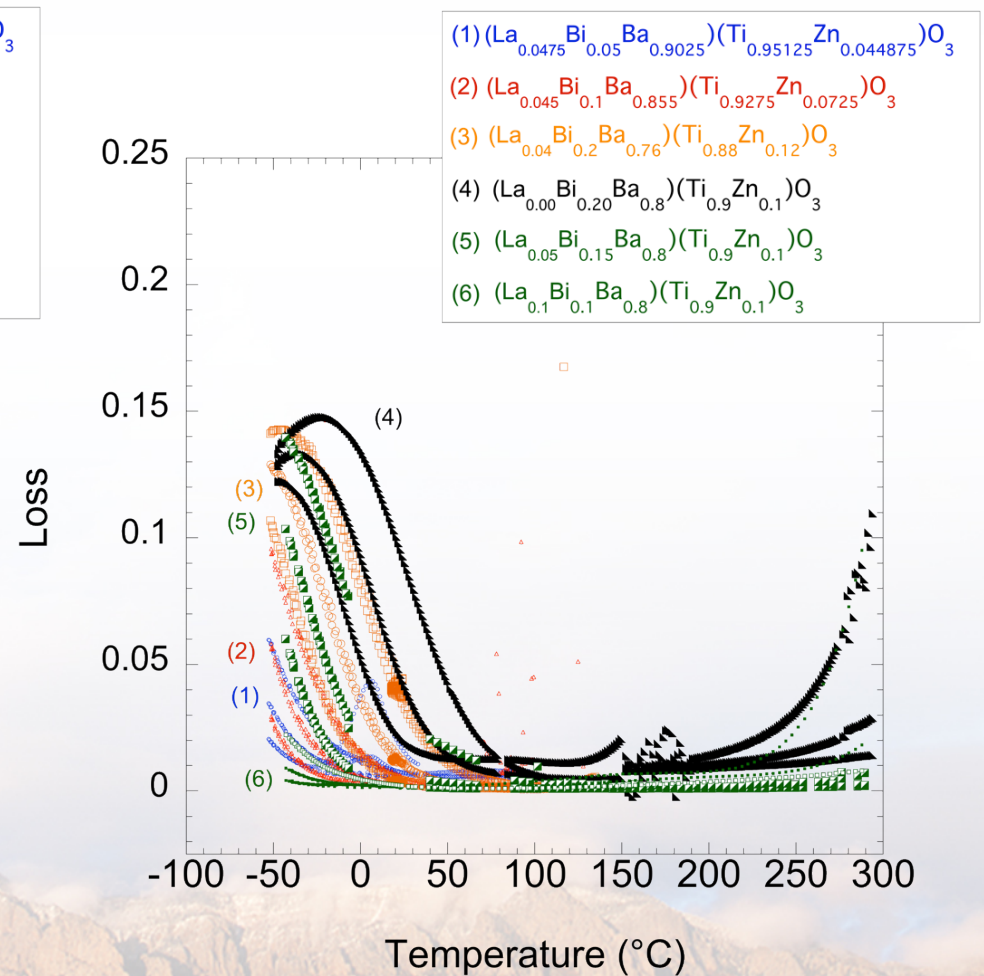
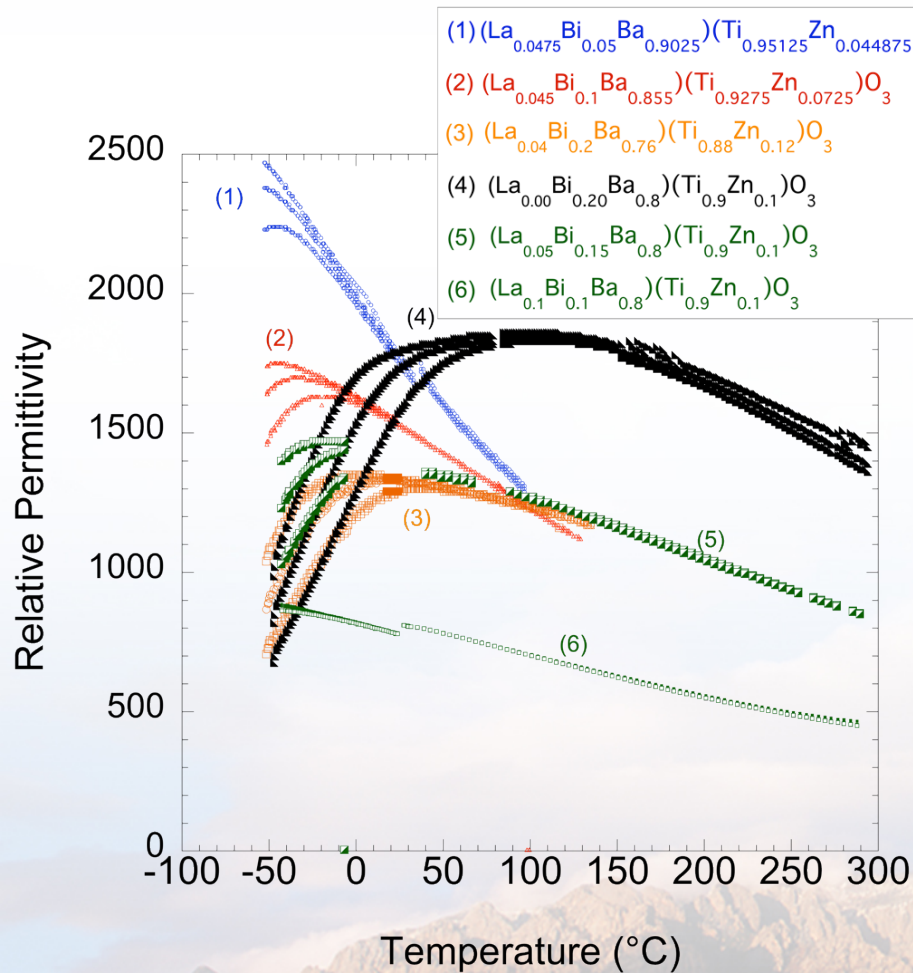
Relaxor Behavior



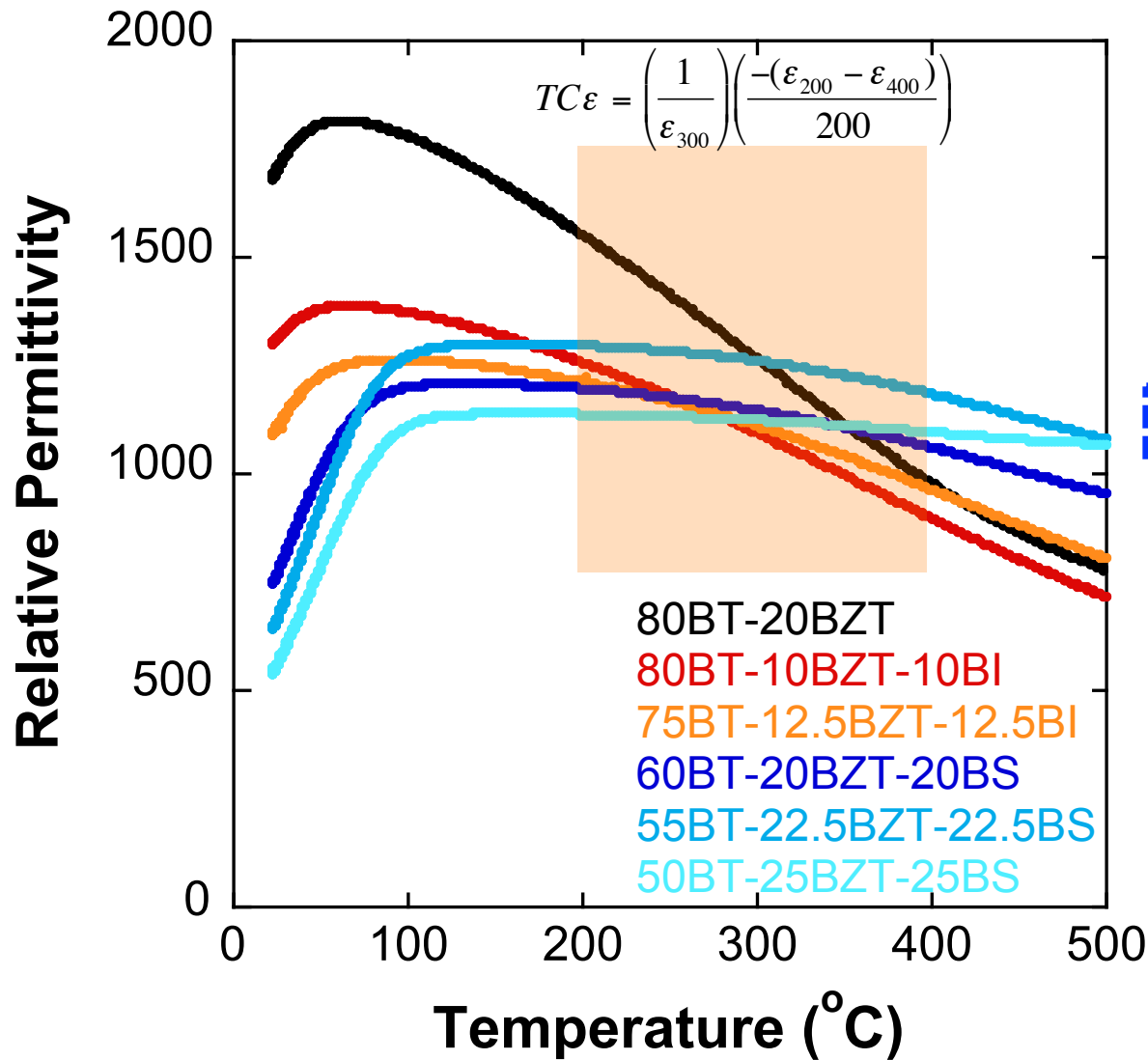
Relaxor Behavior Stable Under Bias



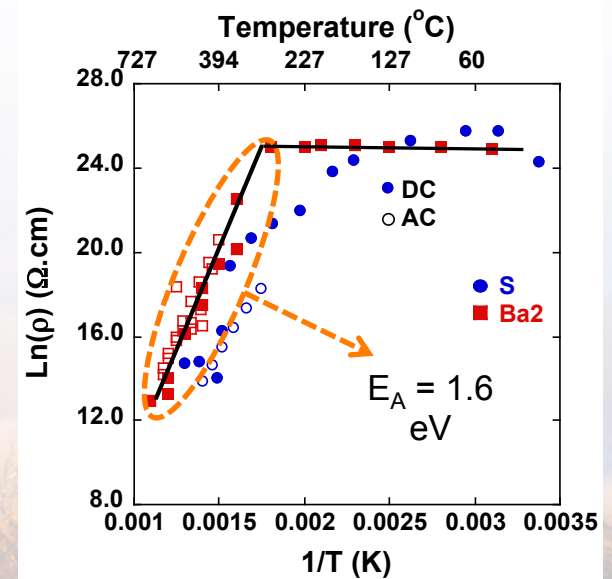
Shifting Relaxor Temperature



Extending Operating Temperatures



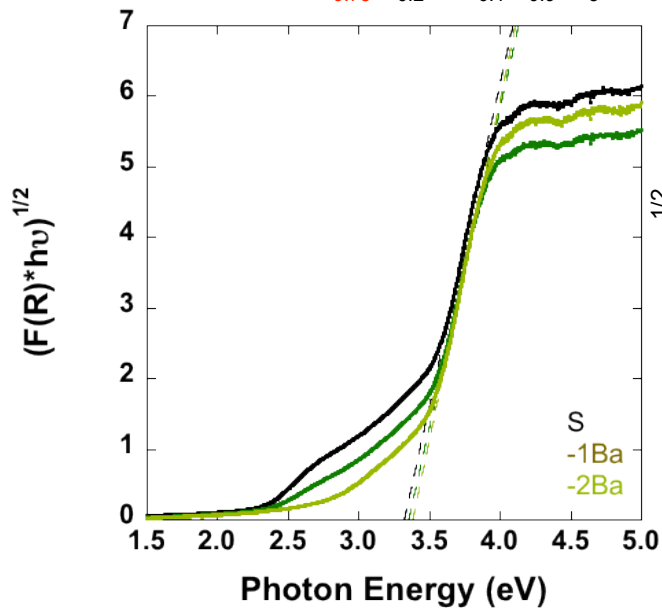
Compound	TCε (ppm/°C)
80BT-20BZT (-2Ba)	-2441
80BT-10BZT-10BI (-2Ba)	-1644
75BT-12.5BZT-12.5BI (-2Ba)	-1114
60BT-20BZT-20BS (-2Ba)	-590
55BT-22.5BZT-22.5BS (-2Ba)	-447
50BT-25BZT-25BS (-2Ba)	-182



Defects and Carriers: Optical

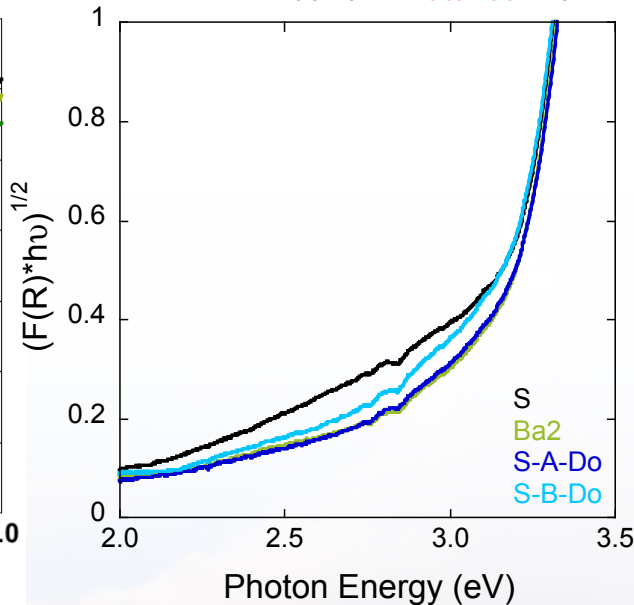
Ba deficiency

- S: nominally-stoichiometric
- Ba-def: $(\text{Ba}_{0.78}\text{Bi}_{0.2})(\text{Zn}_{0.1}\text{Ti}_{0.9})\text{O}_3$



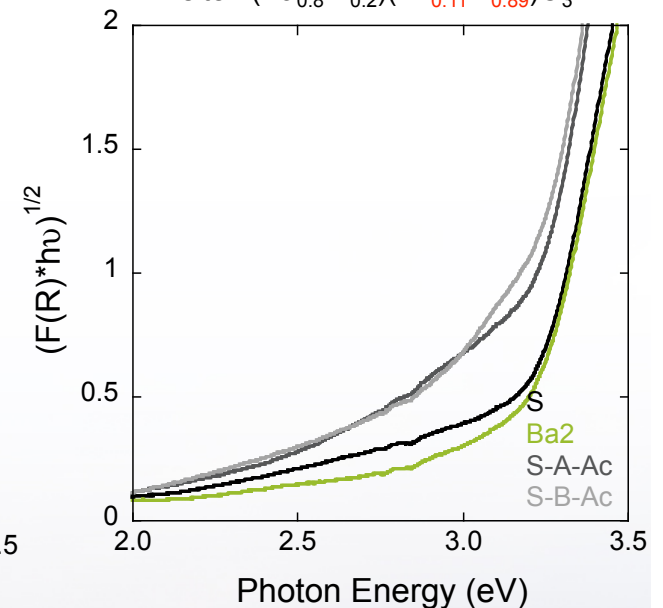
Donor

- A-site: $(\text{Ba}_{0.78}\text{Bi}_{0.22})(\text{Zn}_{0.1}\text{Ti}_{0.9})\text{O}_3$
- B-site: $(\text{Ba}_{0.8}\text{Bi}_{0.2})(\text{Zn}_{0.09}\text{Ti}_{0.91})\text{O}_3$



Acceptor

- A-site: $(\text{Ba}_{0.82}\text{Bi}_{0.18})(\text{Zn}_{0.1}\text{Ti}_{0.9})\text{O}_3$
- B-site: $(\text{Ba}_{0.8}\text{Bi}_{0.2})(\text{Zn}_{0.11}\text{Ti}_{0.89})\text{O}_3$

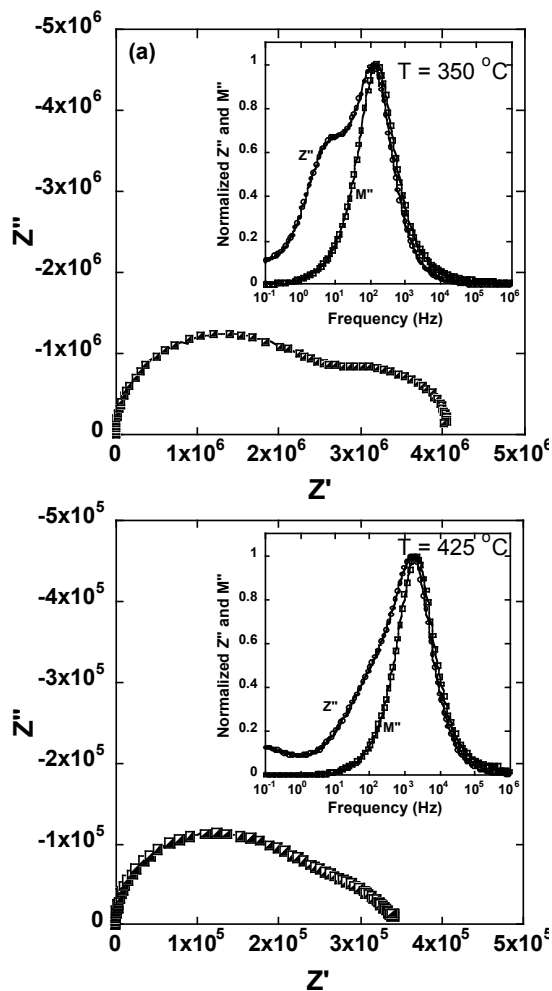


	E_g (eV)
S	3.162
Ba2	3.174

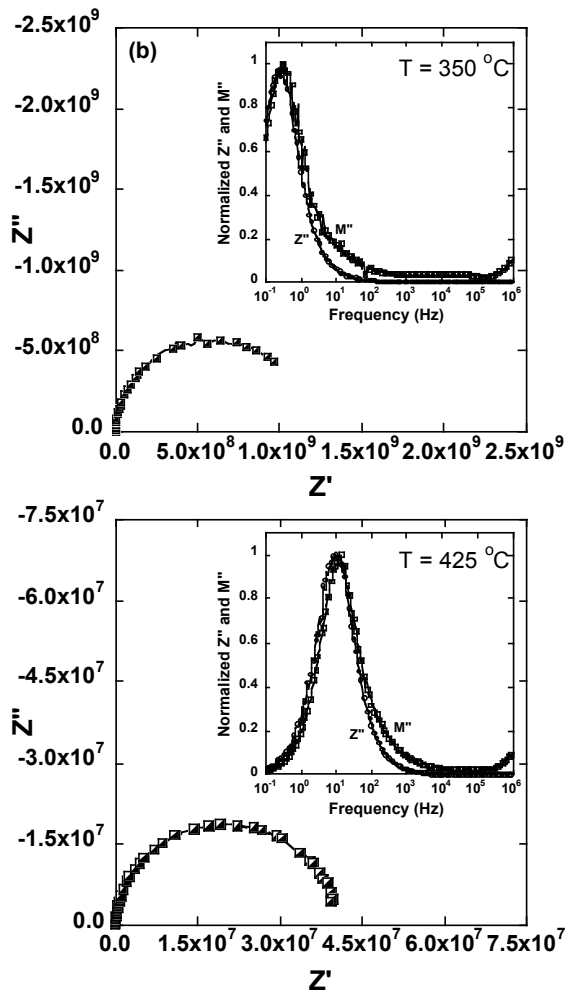
Urbach tail offers qualitative information about mid-gap defect states

Defects and Carriers: Electrical

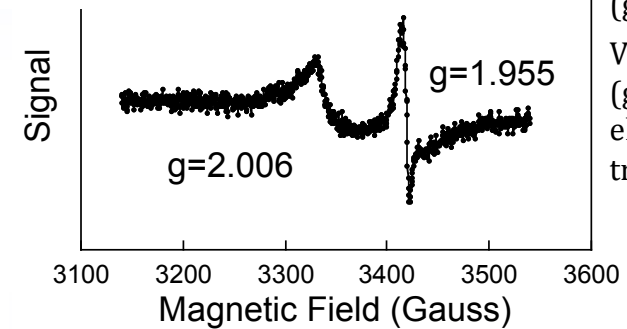
Stoichiometric



2% Ba-deficient

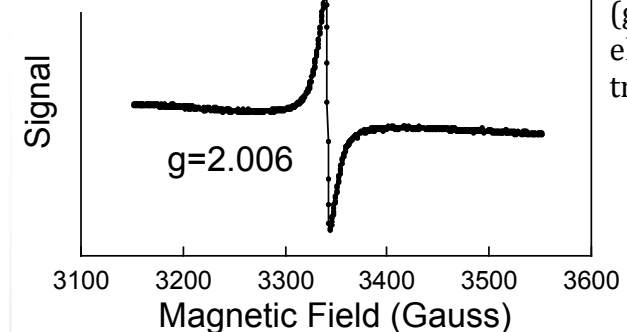


Stoichiometric



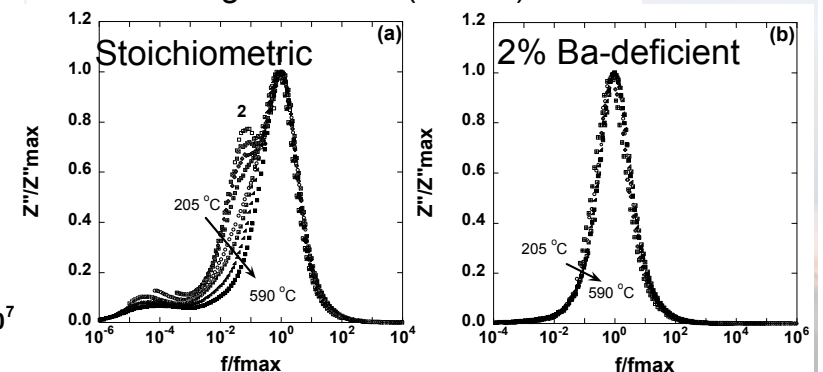
$\text{Ti}^{3+}-\text{V}_0$
($g=1.955$)
 $\text{V}_{\text{Ba}}-\text{V}_0$
($g=2.006$) =
electron
trapped site

2% Ba-deficient



$\text{V}_{\text{Ba}}-\text{V}_0$
($g=2.006$) =
electron
trapped site

*EPR run
at 77K*



Summary

- 'Frustrated' perovskite solid solutions continue to offer exciting opportunities for capacitor applications
- Studies into mechanisms are ongoing; new insights into unusual relaxor behavior could open up more avenues for optimization

