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Oxygen vacancy migration and impact on high voltage DC polarization in $BaTiO_3$-$Bi(Zn,Ti)O_3$

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S10: Structure of Defects and Defect Mediated Properties
EMA-101-2023: 3:15 – 3:30 pm

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U.S. DEPARTMENT OF ENERGY

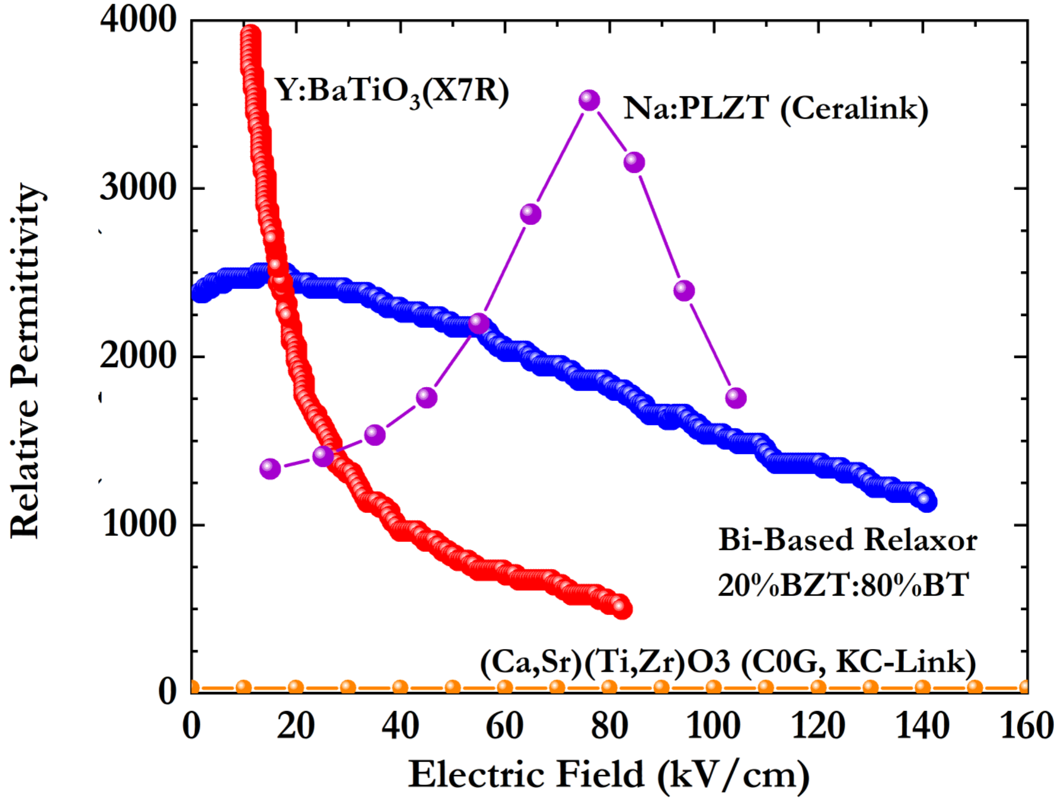
NNSA

High Permittivity in High Electric Field and Temperature

20BZT-BT: 20% $Bi(Zn_{0.5}Ti_{0.5})O_3$-80% $BaTiO_3$

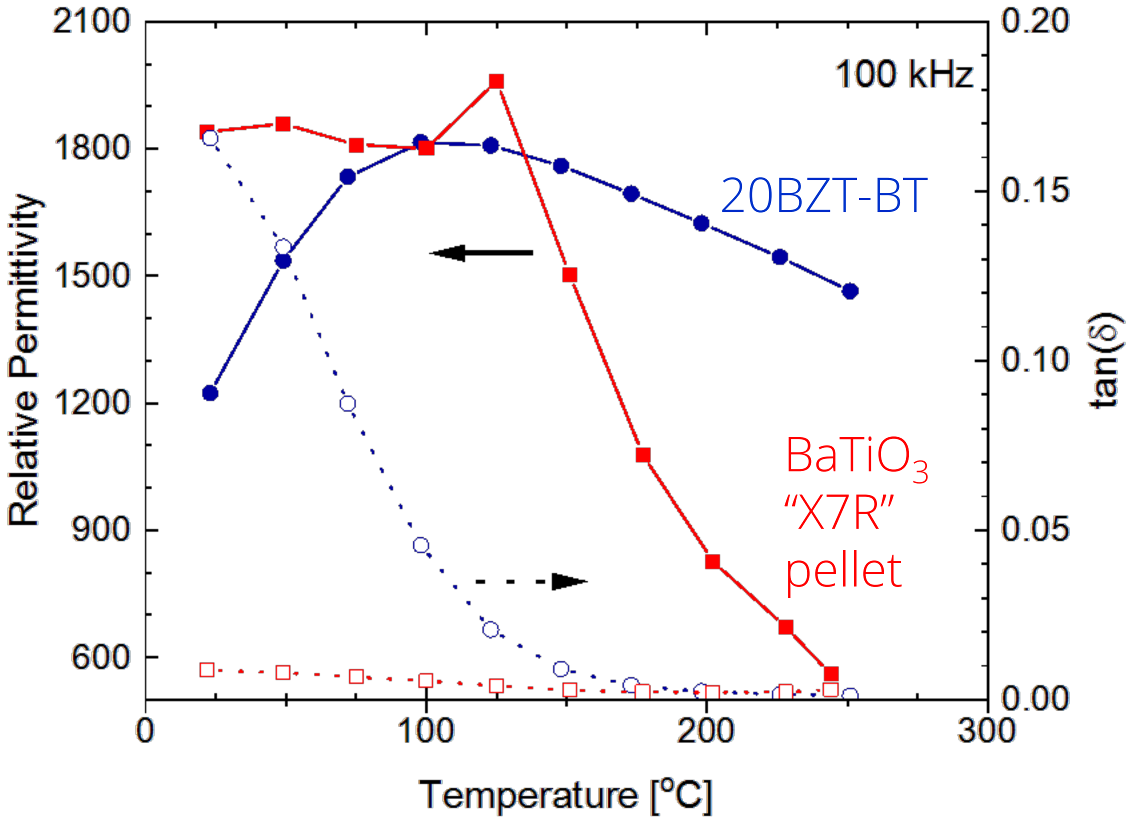
High and less variable permittivity at high electric field and temperature, desirable for high power conversion applications

High permittivity at >120 kV/cm



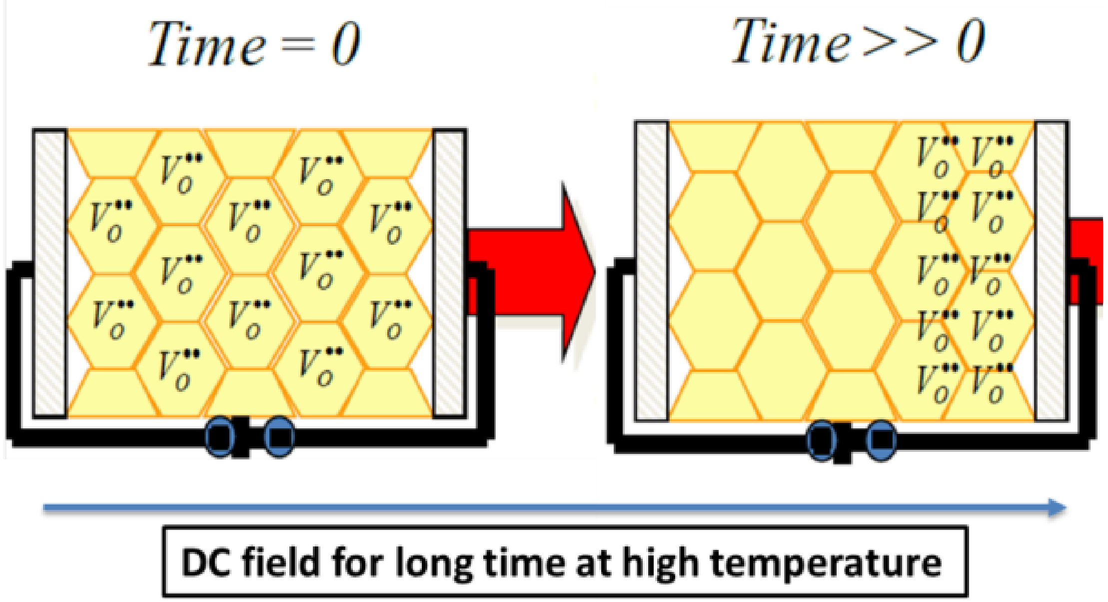
Beuerlein et al., J. Am. Ceram. Soc., 99 (2016) 2849

High permittivity at >200°C at 100 kHz



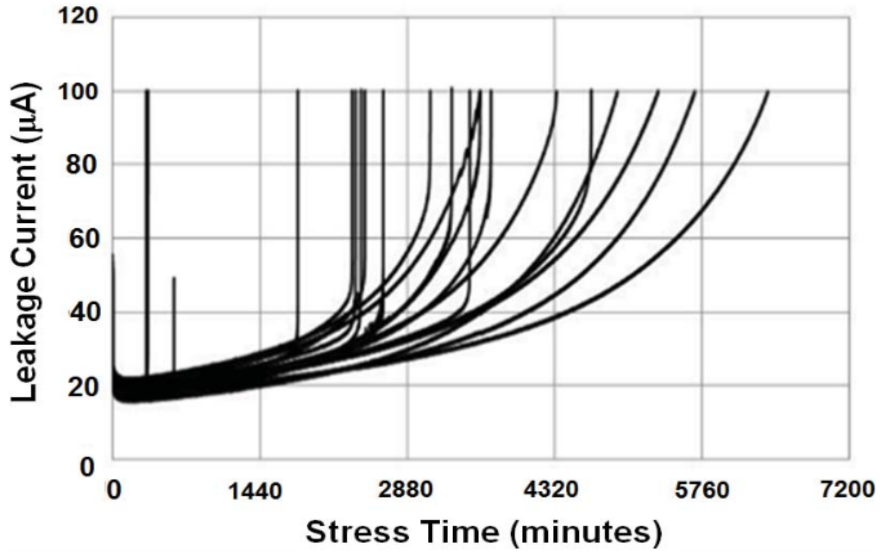
Oxygen Vacancy Migration Can Limit DC Lifetime

DC bias → oxygen vacancy ($V_O^{\cdot\cdot}$) migration
- Change in electron and hole concentration
- Increase in bulk and or electrode leakage current



R. Maier, Penn. State PhD Thesis (2014)

Accelerated DC Lifetime for BME X7R MLCC's



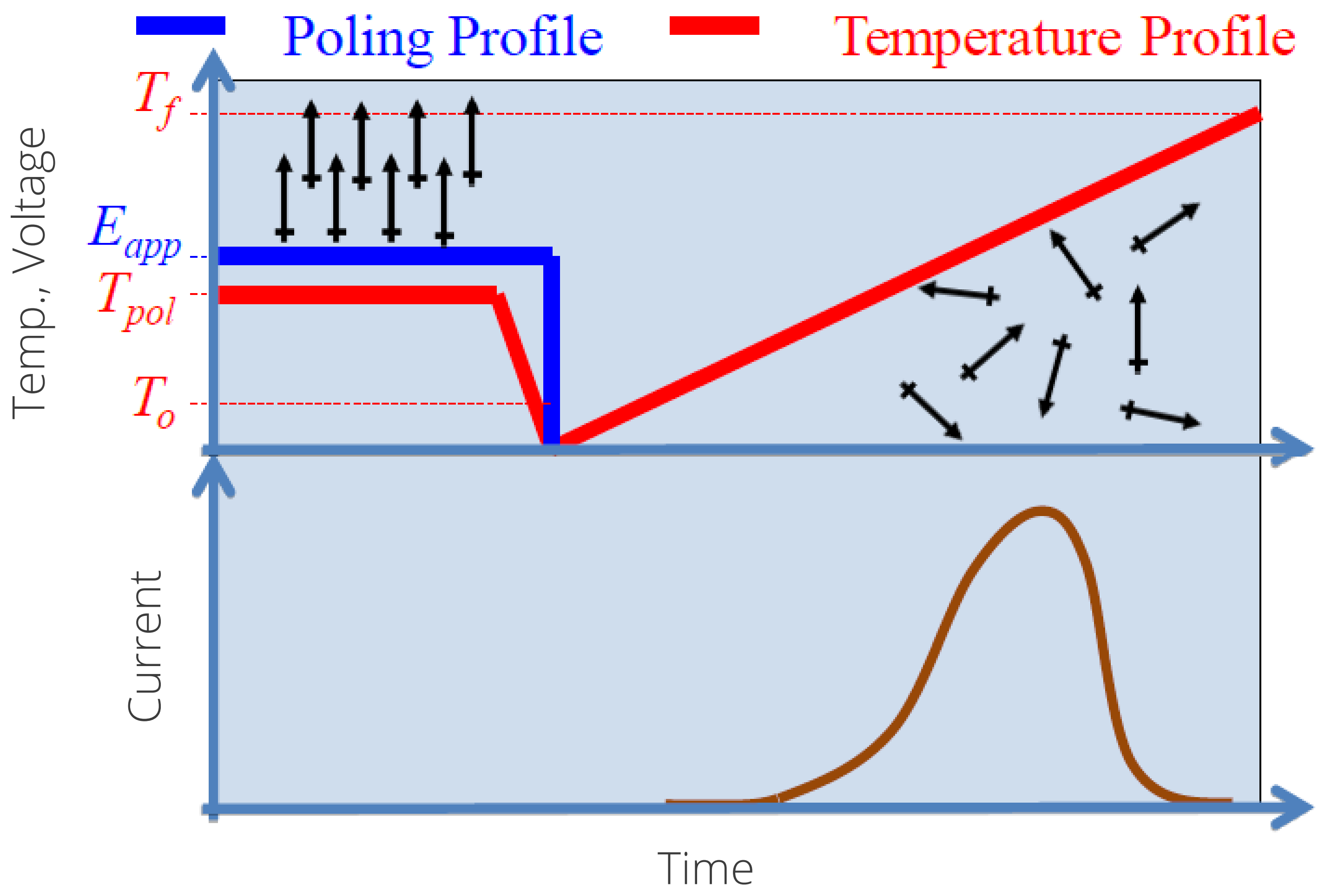
Accelerated test (5x Vr)
0.47 uF, 50 V Rated, 0805, 250 V, 155 °C

D. Liu, IEEE Tran. Comp. Pack. Man. Tech. 5 (2015) 40

DC lifetime and degradation modes uncharacterized in BZT-BT

Thermally Stimulated Depolarization Current (TSDC)

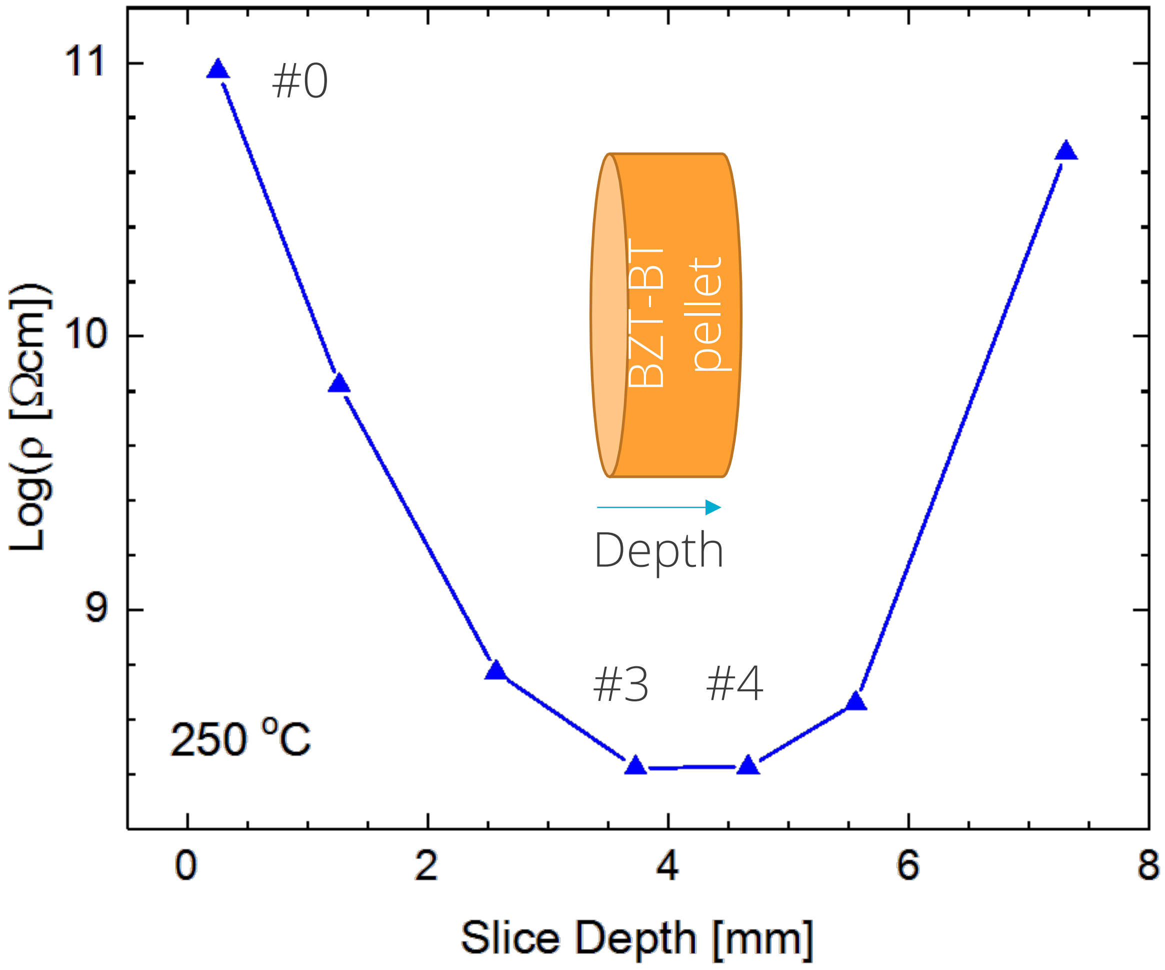
$V_O^{\cdot\cdot}$ are typically not majority charge carriers → probe mobile point defects with TSDC



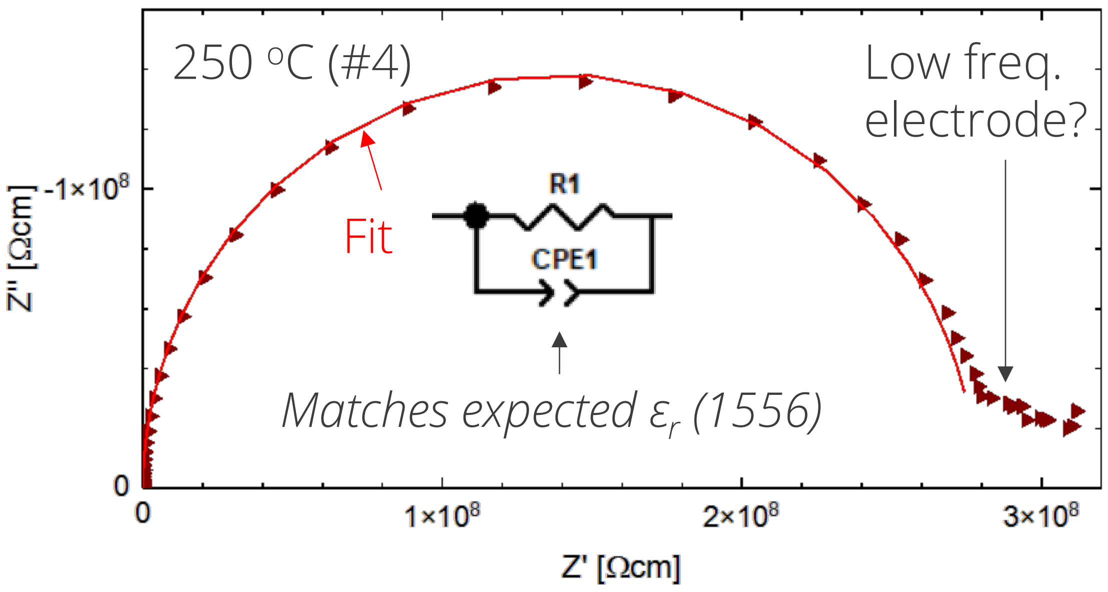
Maier, Penn State PhD Thesis (2014)

Large Resistivity Change Across Thickness→ $\Delta V_O^{\cdot\cdot}$?

Bi-rich BZT-BT: $(Bi_{0.22}Ba_{0.78})(Zn_{0.1}Ti_{0.9})O_3$ (Donor doped to suppress $[V_O^{\cdot\cdot}]$)

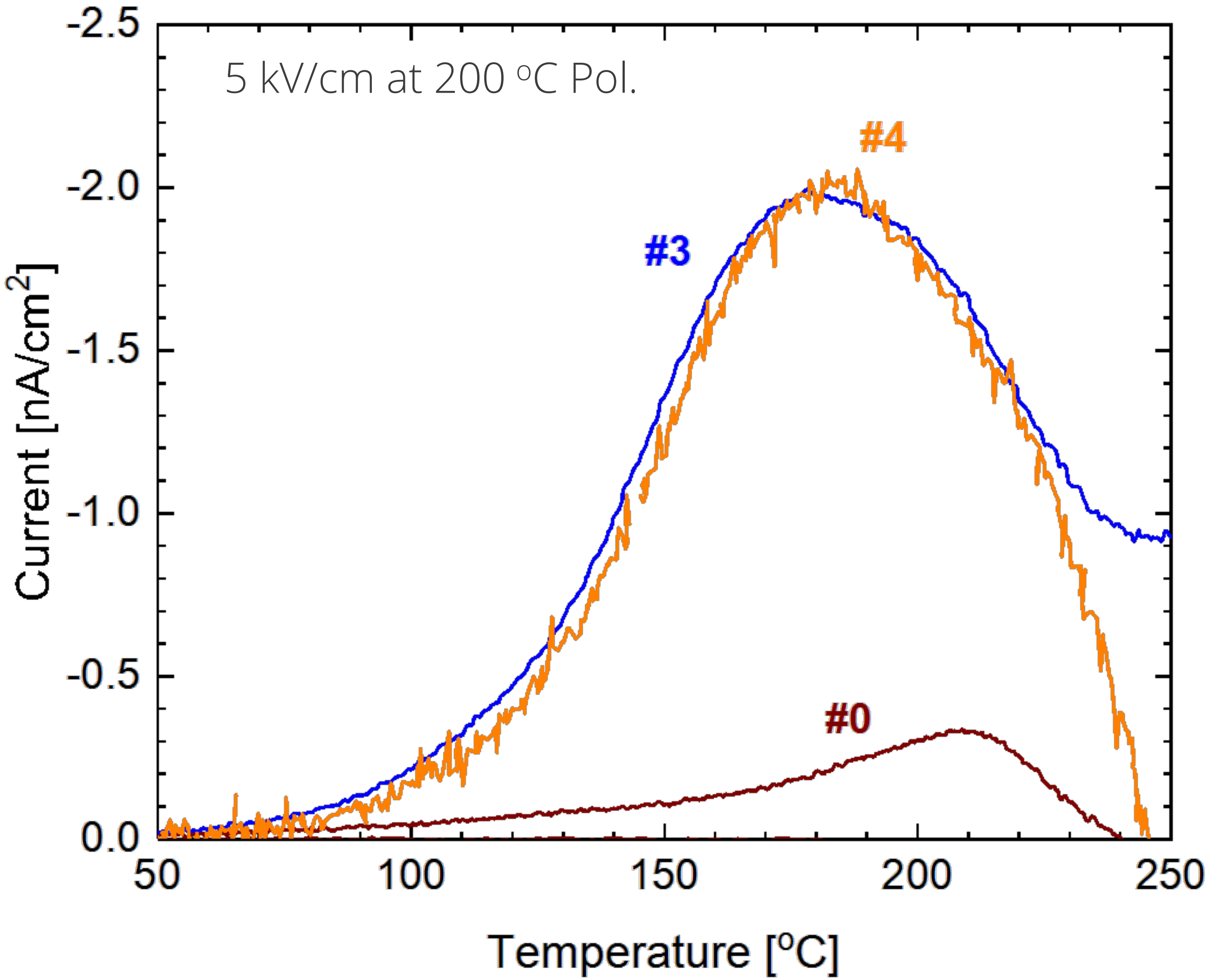


Impedance spectroscopy



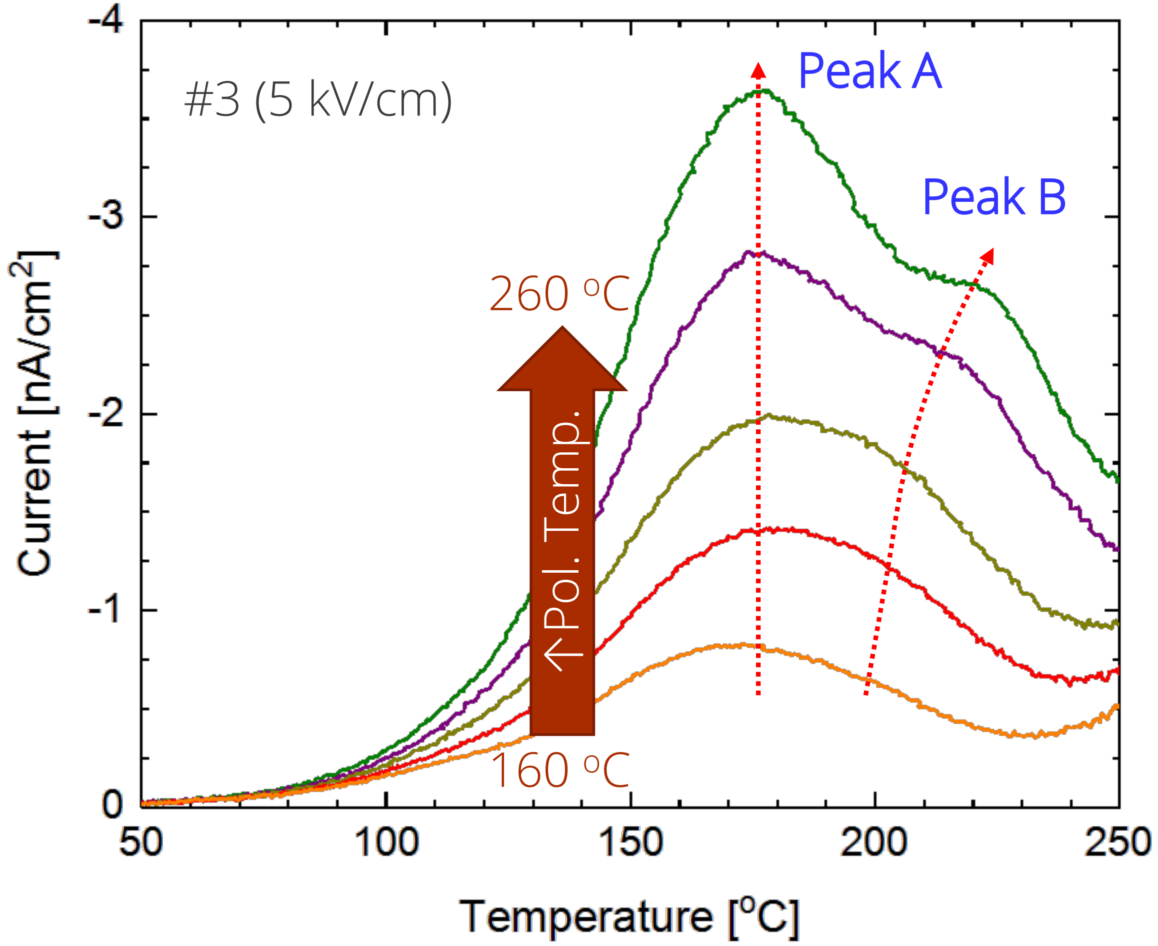
→ Opportunity to examine $V_O^{\cdot\cdot}$ impact on TSDC and DC lifetime!

Largest TSDC Response for Lowest Resistance Samples



Very large TSDC near center of sample, consistent with significant $V_O^{\cdot\cdot}$ concentration

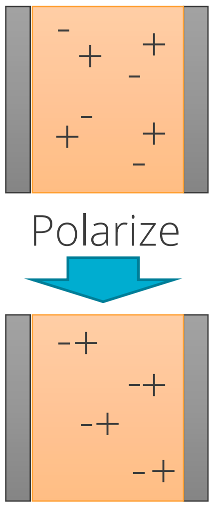
Polarization Temperature Dependence of TSDC



Max. peak area = ~80 μC/cm³ → ~0.006 ppm [$V_O^{\bullet\bullet}$]

Peak A

Dipole defects (e.g., $V_O^{\bullet\bullet}$-V_{Ba}'')

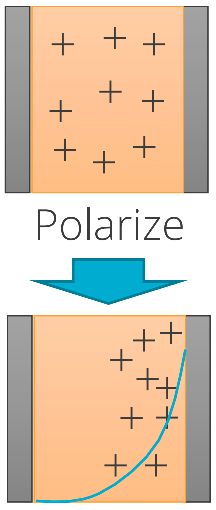


Defects "depolarize" at single temperature

→ *No T dependence*[1]

Peak B

Space charge defects (e.g., $V_O^{\bullet\bullet}$)

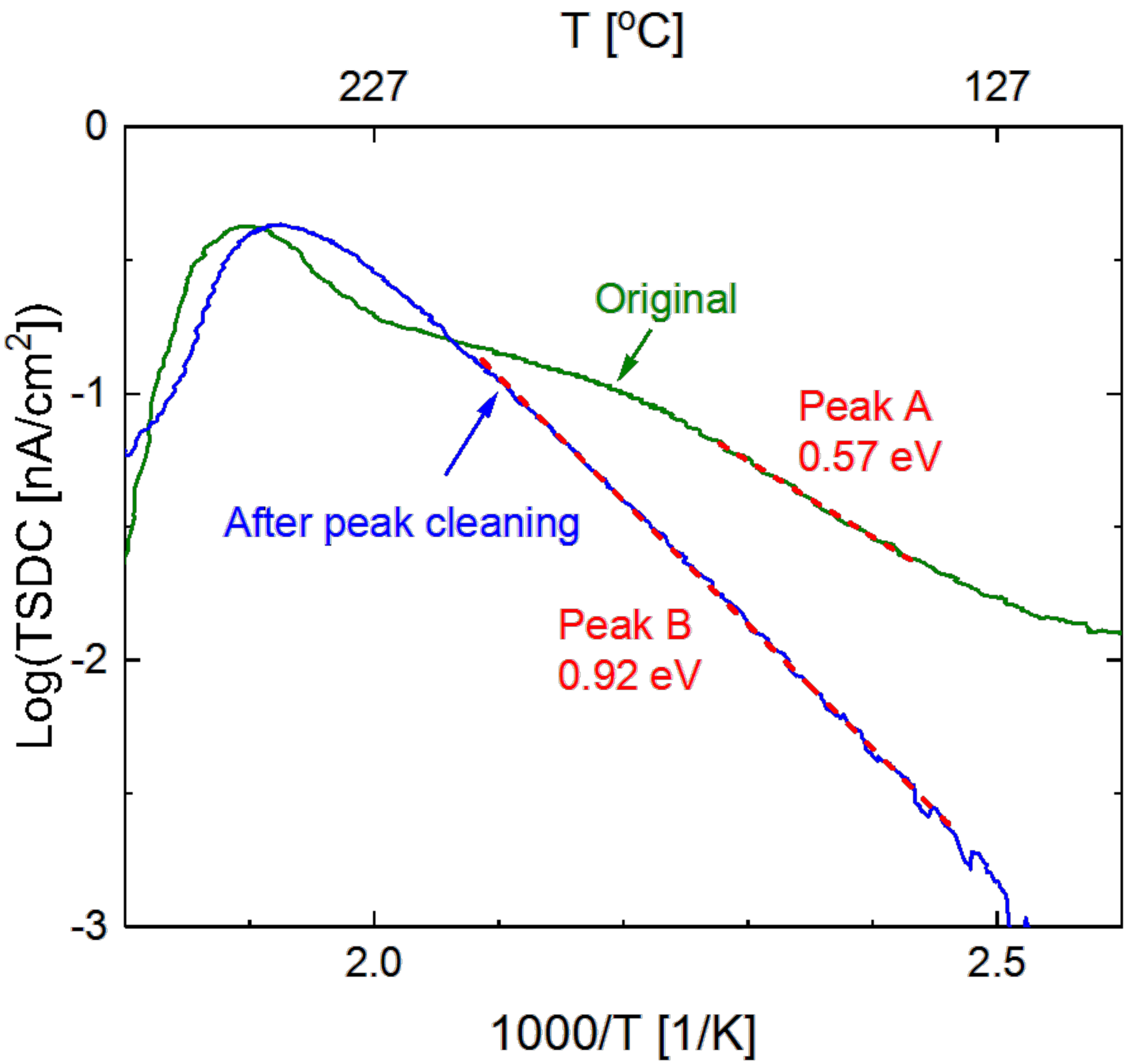


Greater concentration gradient → more time/temp. to depolarize

→ *T dependence*[1]

[1]Liu, Penn State PhD Thesis (2009)

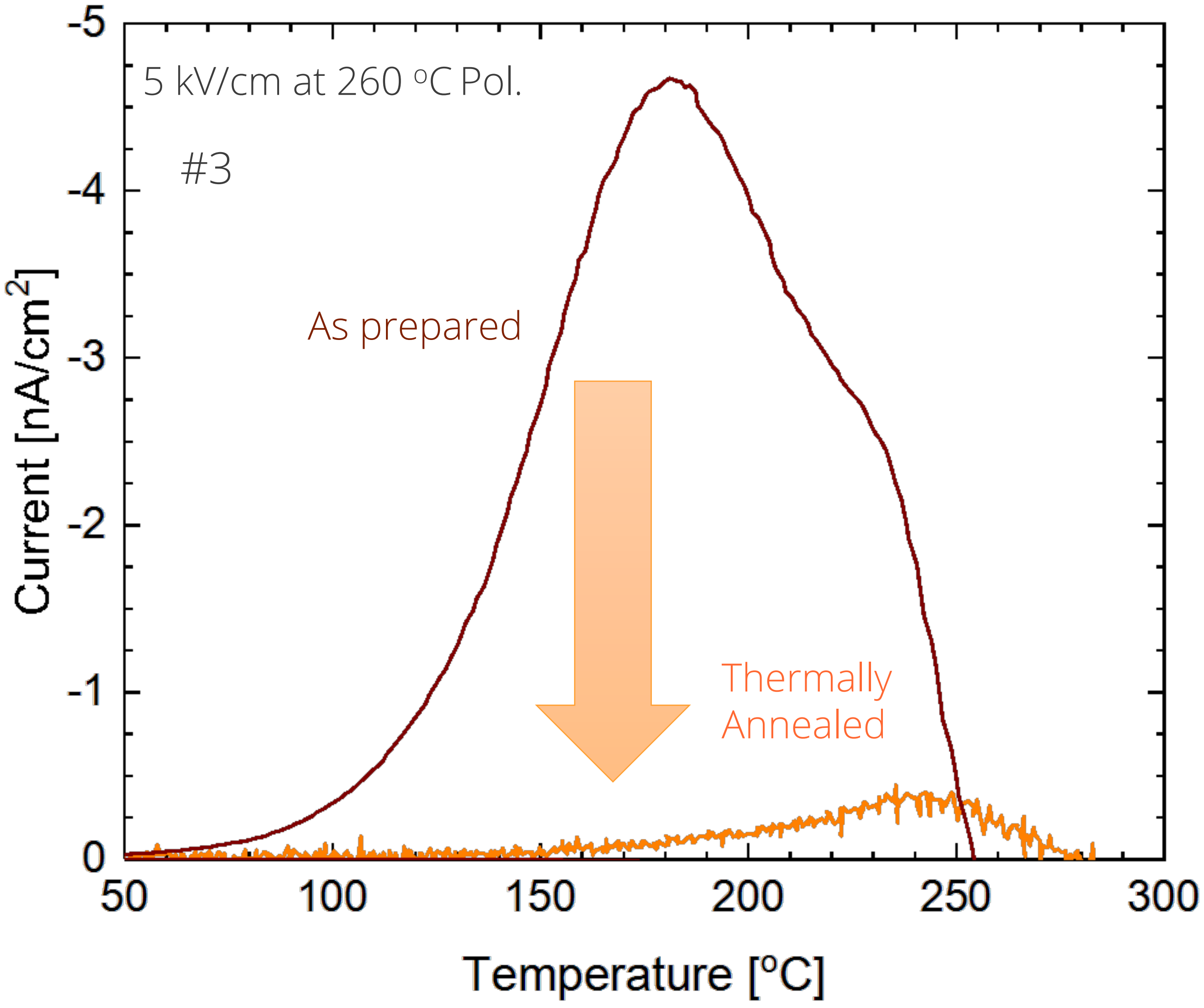
Activation Energies (E_A) Consistent with Dipolar and Space Charge



- E_A ~ 0.7 eV typical of $V_O^{\cdot\cdot}$ grain diffusion
- Low E_A of Peak A → consistent with dipolar or grain conduction
- Larger E_A Peak B → possible space charge boundary blocking conduction

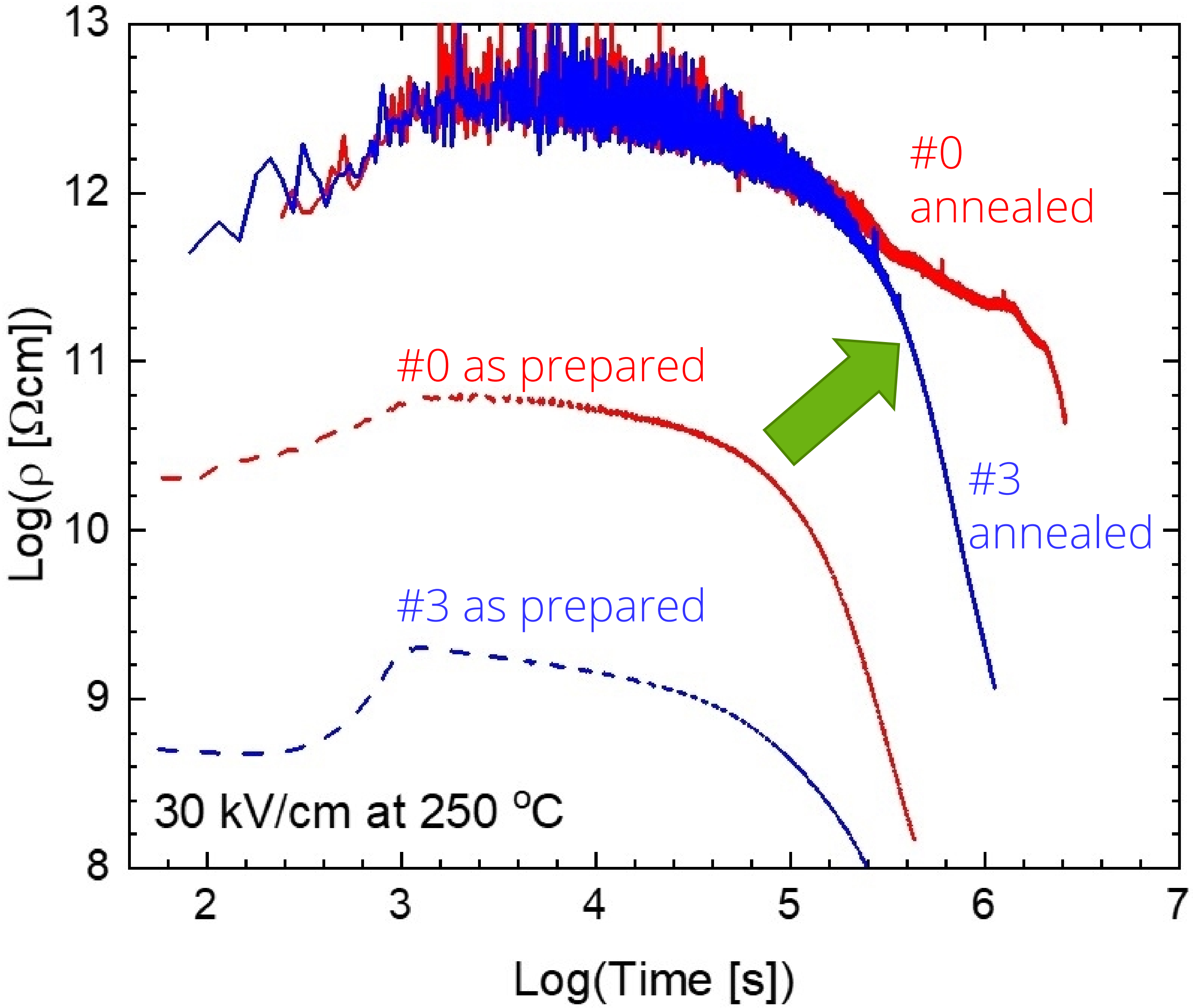
Note: Ba-deficient BZT-BT sample shown

Thermal Annealing Decreases TSDC Response

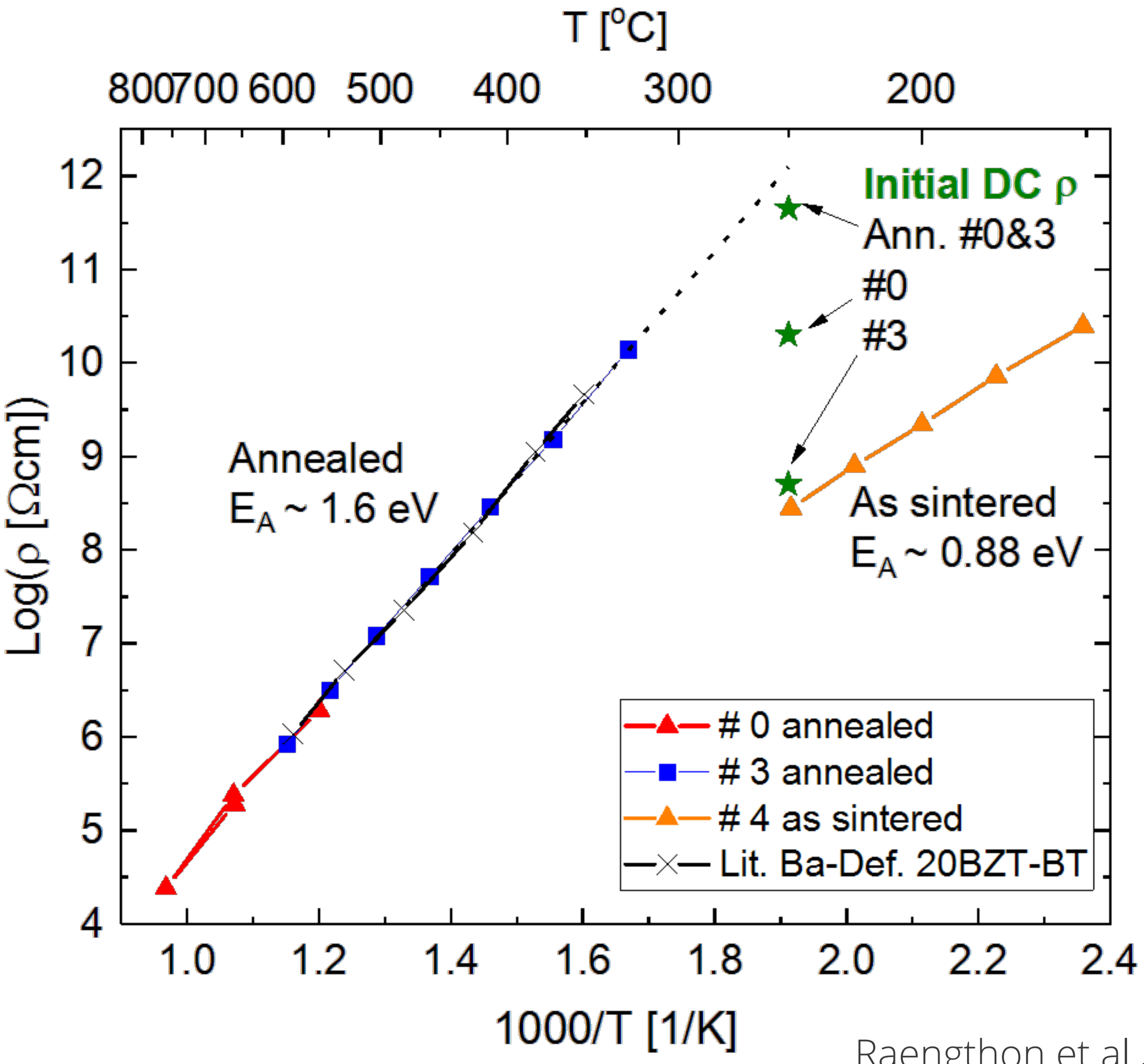


- Thermal anneal: ~1 day at 800 °C in air
- Thermal annealing dramatically reduces TSDC response, consistent with TSDC probing $V_O^{\cdot\cdot}$

DC Lifetime Increased with Annealing



Oxide Ion Conductivity at Low Temperature

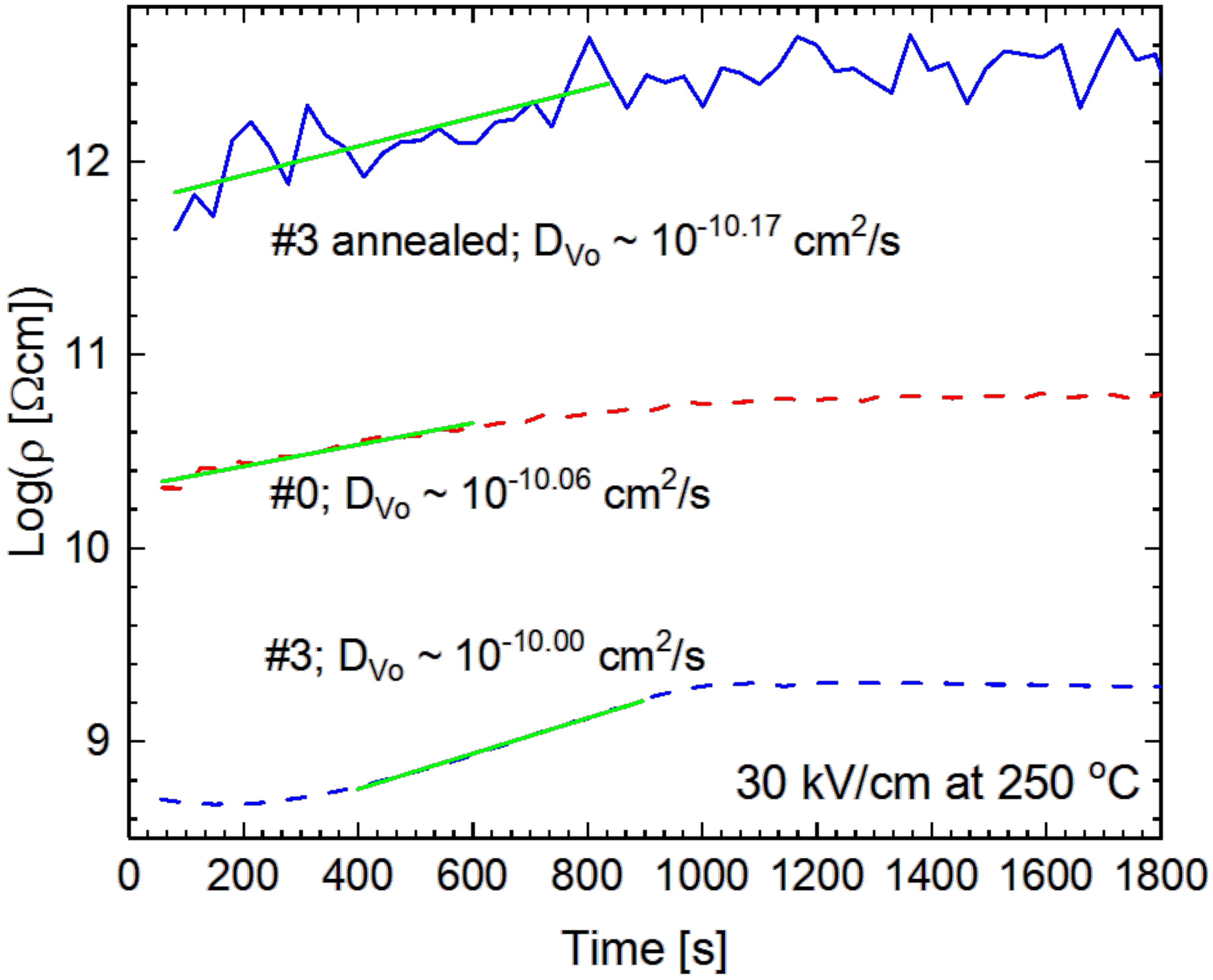


- Intrinsic electronic conduction at high temperature
- At low temp. all samples are more conductive than intrinsic electronic
  - E_A consistent with oxide ion conduction

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

Initial $V_O^{\cdot\cdot}$ Polarization Current, Then Electronic

- Fit drift of $V_O^{\cdot\cdot}$ → $\rho(t) = \rho_o \exp(t/\tau)$
- Estimate $D_{Vo} \sim kTl/(2q\tau E)$



D_{Vo} lower than lit. ($BaTiO_3$ $D_{Vo} \sim 10^{-9}$ (E_A = 0.7 eV)[1])

→ *Consistent with defect association*

Estimate $[Vo^{\cdot\cdot}] = \sigma kT/(4q^2 D_{Vo})$

$[Vo^{\cdot\cdot}]$

#0 ~ 0.86 ppm

#3 ~ 30 ppm

Annealed #0 & 3 ~ 0.05 ppm

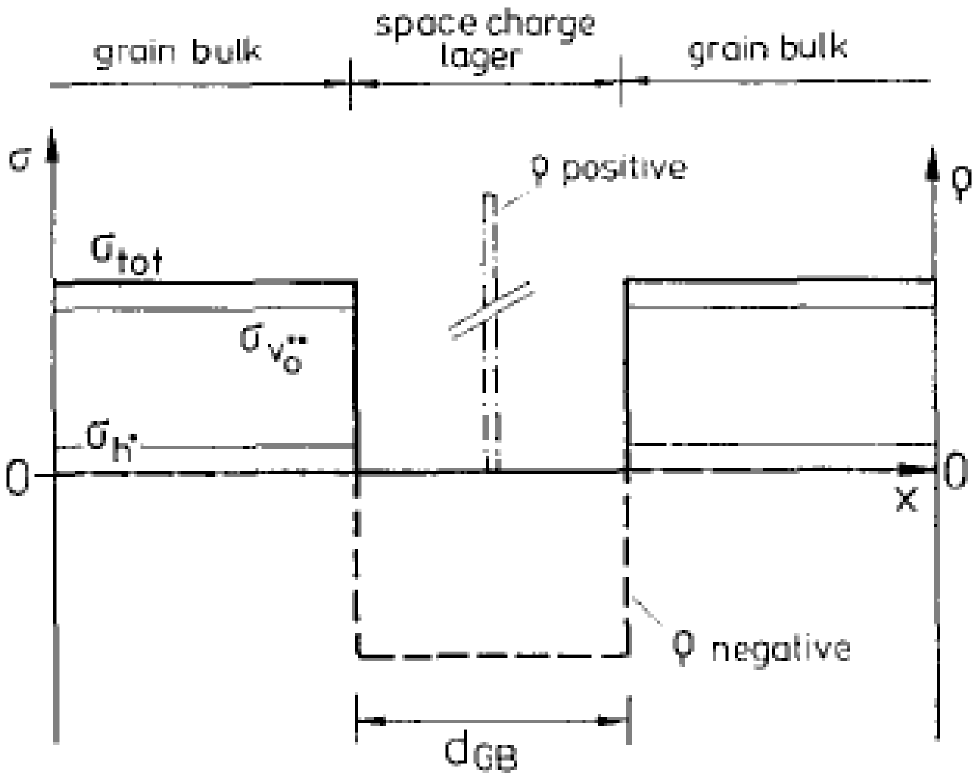
$[V_O^{\cdot\cdot}]$ low, but not unreasonable

At longer times, formation of n and p regions → electronic conduction and ultimately shorting[2]

[1]Kessel et al., Phys. Chem. Chem. Phys. 17 (2015) 12587

[2]Waser et al., J. Am. Ceram.Soc. 73 (1990) 1654

Space Charge Boundary



Waser, Solid State Ionics, 75 (1995) 89

- Positively charged boundaries suppress [Vo¨] → increased ionic resistance

- As sintered samples have high [e'] which may screen barrier
  - → more conductive as sintered samples
  - → increase in resistivity with annealing

Conclusions

- $V_O^{\cdot\cdot}$ lead to significantly shorter DC lifetimes in BZT-BT, at low estimated concentrations
- Resistivity is increased by annealing for long lifetime – role of space charge
- Annealing likely requires oxidizing atmosphere → MLCCs using base metal electrodes (e.g., Ni) are likely incompatible with BZT-BT
- The very low intrinsic electronic conductivity leads to predominant ionic conductivity in BZT-BT in typical application temperatures (atypical of other capacitor materials)

Acknowledgements

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