The role of oxygen vacancies on DC lifetime and TSDC in $Bi(Zn,Ti)O_3$-$BaTiO_3$ (BZT-BT)

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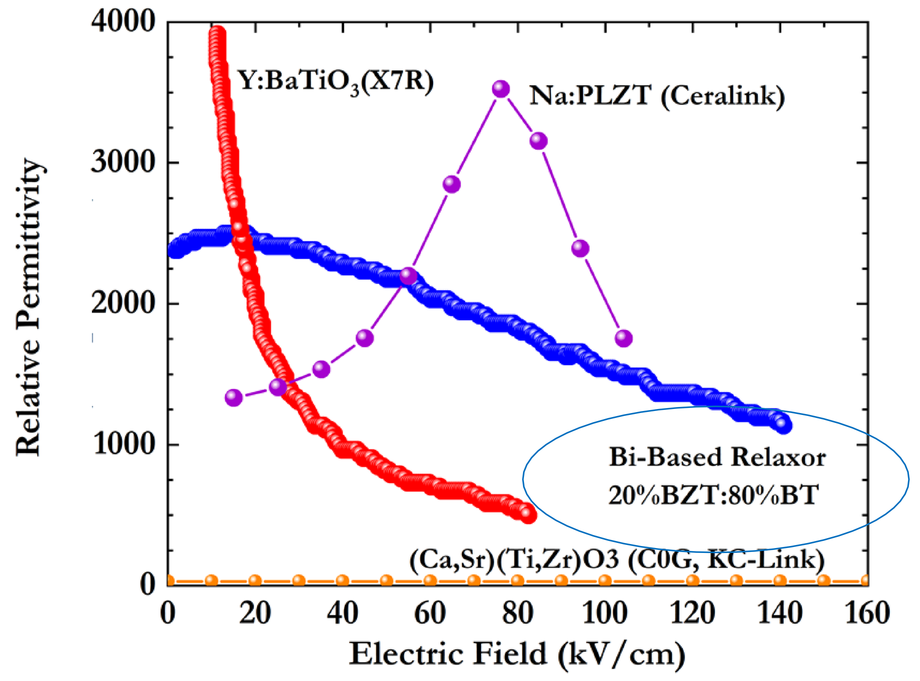
Introduction

High permittivity in high electric field and temperature applications



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

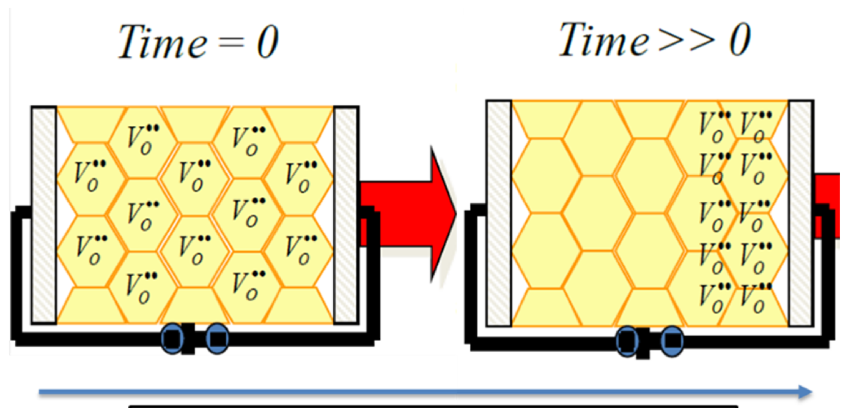
20BZT-BT: 20% $Bi(Zn_{0.5}Ti_{0.5})O_3$-80% $BaTiO_3$ has high and less variable permittivity at high electric field and temperature, desirable for high power conversion applications

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

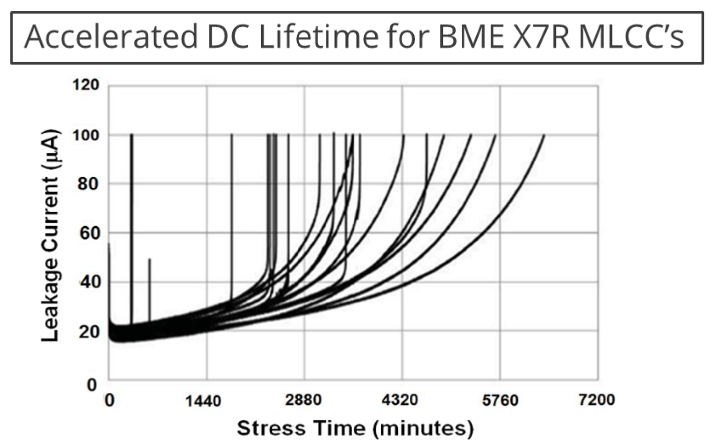
Oxygen vacancy migration can limit DC lifetime

DC bias in operation → oxygen vacancy ($V_O^{\bullet\bullet}$) migration

- Electron and hole concentration gradients created across sample
- Increase in bulk and or electrode leakage current



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

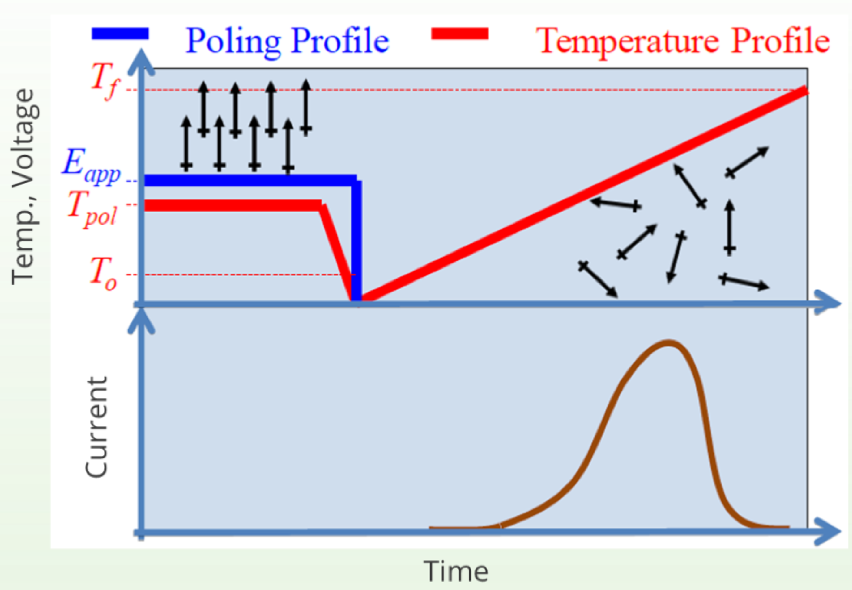


Accelerated test (5x Vr)
0.47 uF, 50 V Rated, 0805, 250 V, 155 °C

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

DC lifetime and degradation modes uncharacterized in BZT-BT

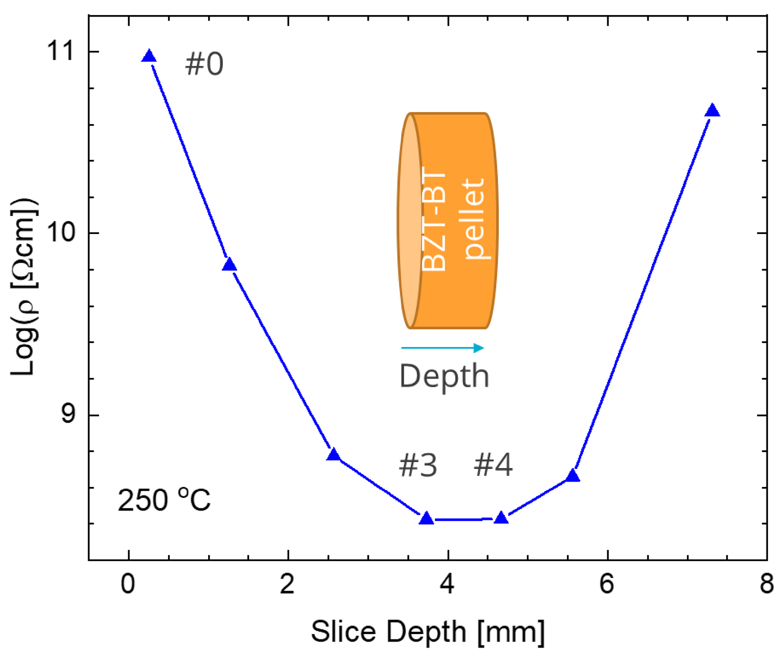
$V_O^{\bullet\bullet}$ are typically not majority charge carriers → probe mobile point defects with thermally stimulated depolarization current (TSDC)

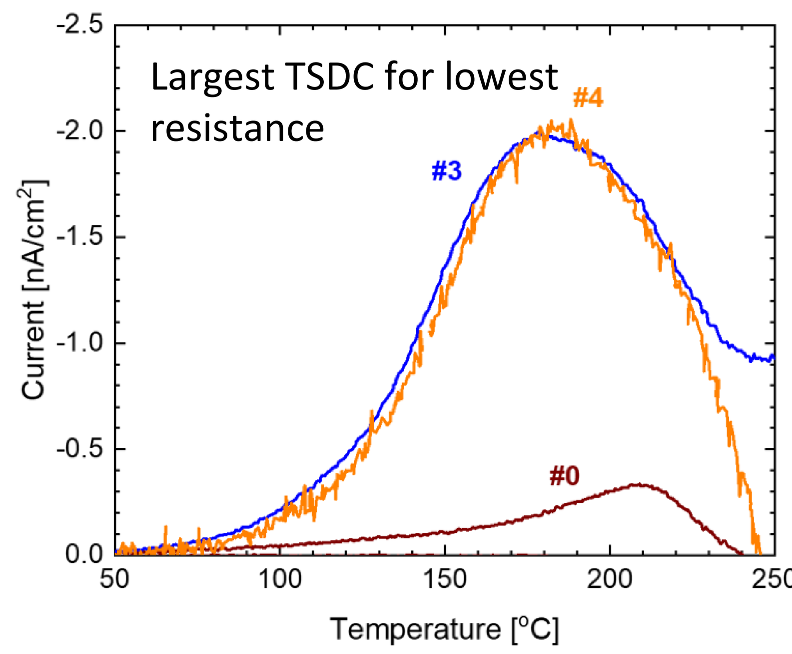


Maier, Penn State PhD Thesis (2014)

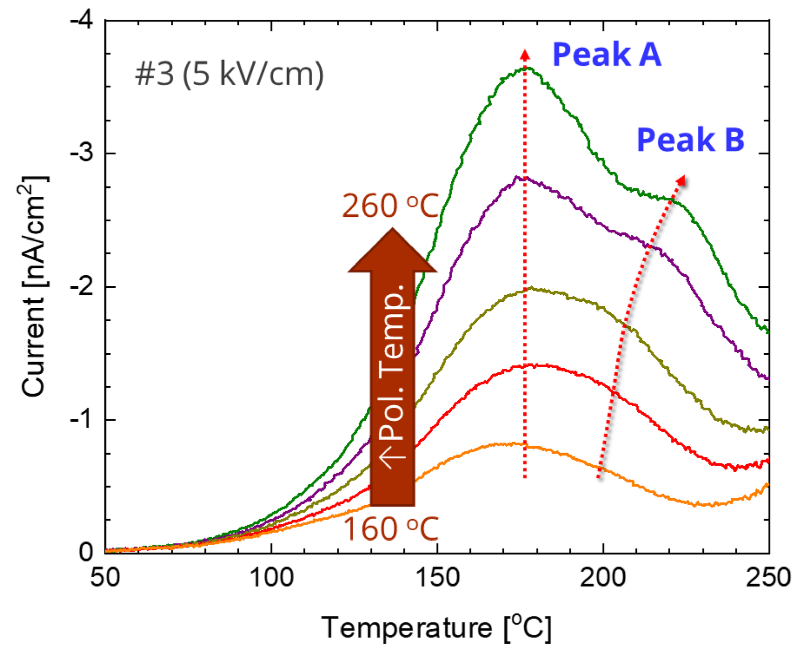
Results

Large resistivity and TSDC change across thickness





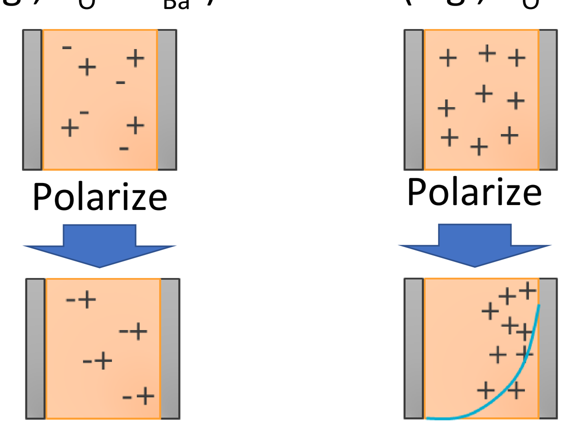
Polarization temperature dependence and mechanism of TSDC



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}'')

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

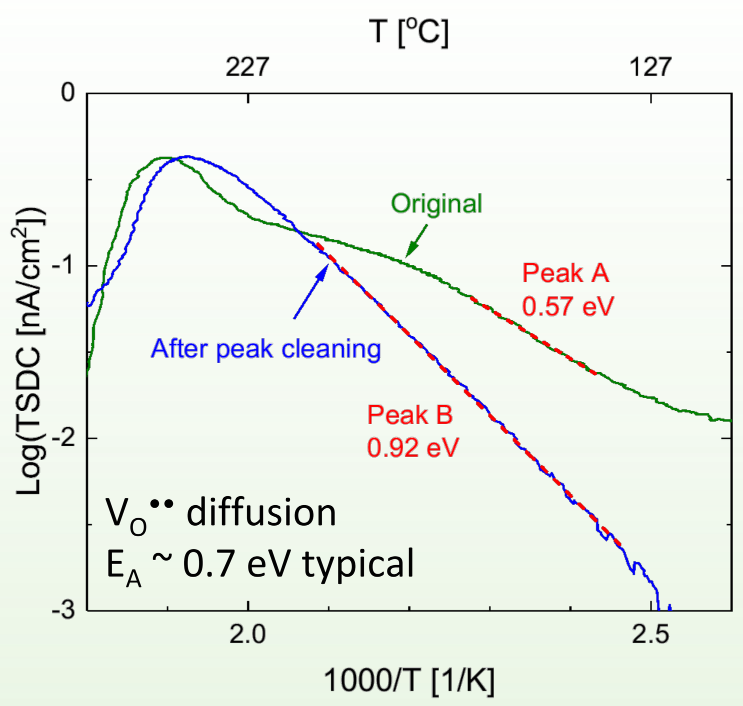


Defects "depolarize" at single temperature
→ *No T dependence*[1]

More time/temp. to depolarize conc. gradient
→ *T dependence*[1]

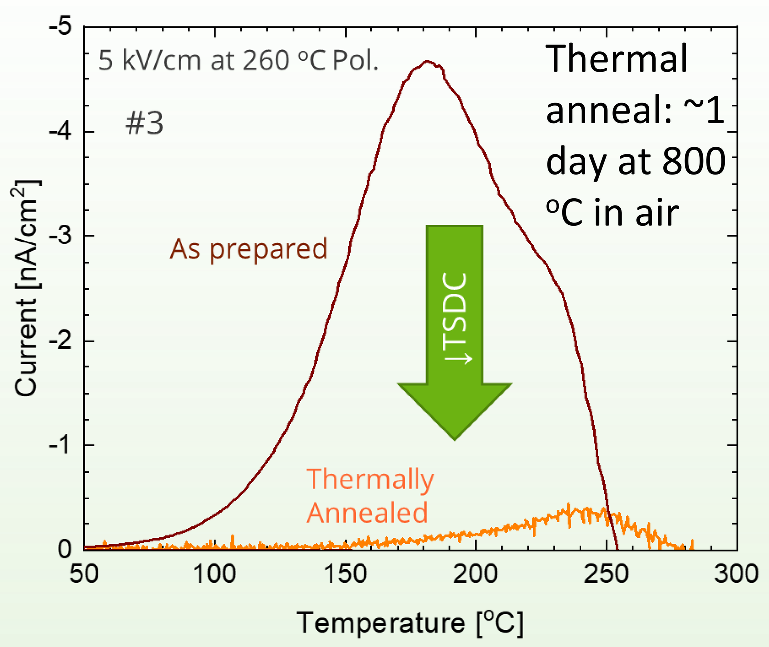
[1]Liu, Penn State PhD Thesis (2009)

Activation Energies (E_A) Consistent with Dipolar and Space Charge



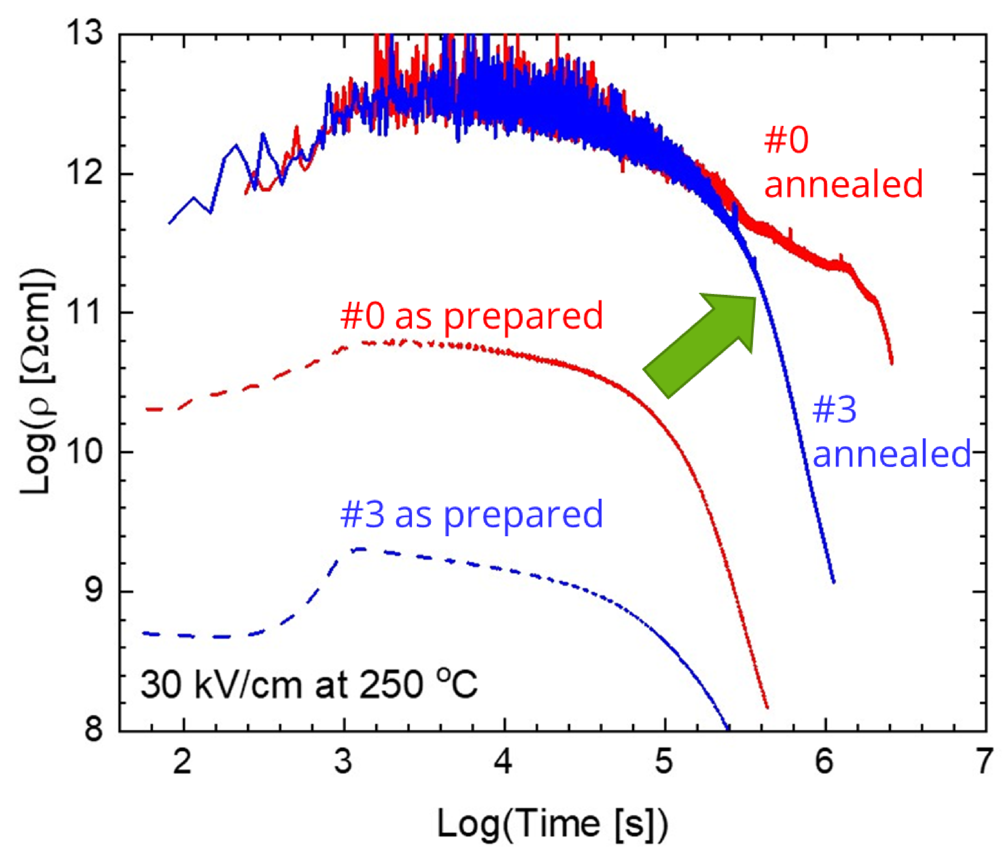
$V_O^{\bullet\bullet}$ diffusion
E_A ~ 0.7 eV typical

Thermal annealing dramatically reduces TSDC response, consistent with $V_O^{\bullet\bullet}$



Thermal anneal: ~1 day at 800 °C in air

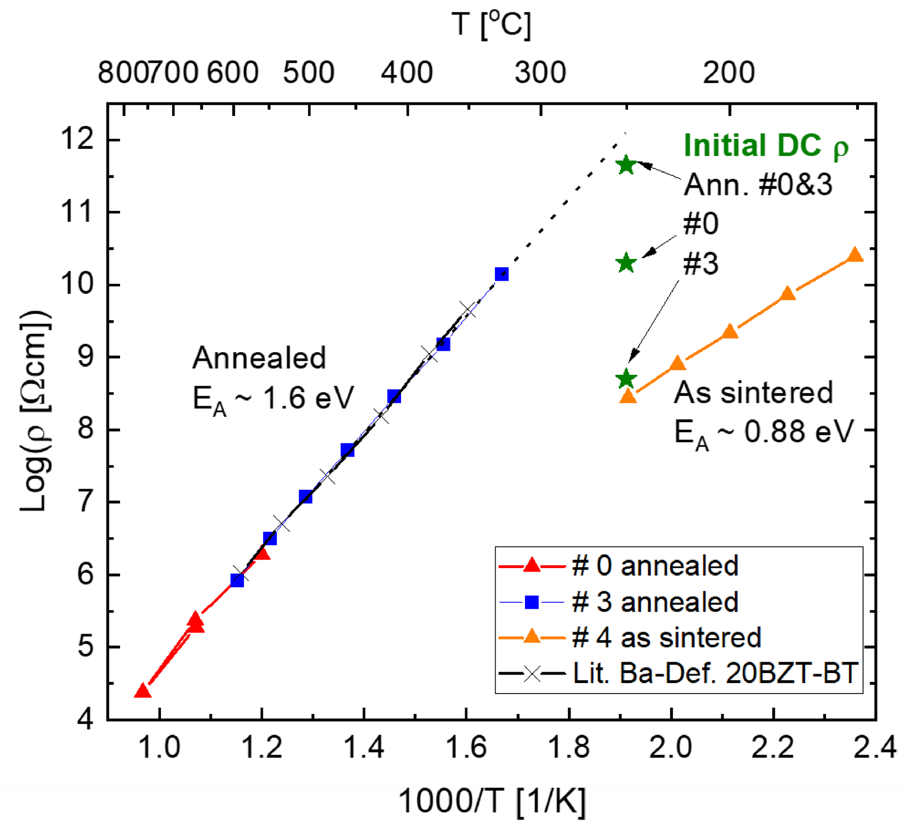
DC lifetime increased with thermal annealing



Thermal anneal: ~1 day at 800 °C in air

Result consistent with decrease in $V_O^{\bullet\bullet}$ concentration after annealing

Possible oxide ion conductivity at low temperature



- Intrinsic electronic conduction at high temperature
- At low temp. all samples are more conductive than intrinsic electronic
- Low T. E_A consistent with oxide ion conduction
- Must also consider possible grain boundary blocking behavior

Conclusions

- $V_O^{\bullet\bullet}$ lead to significantly shorter DC lifetimes in BZT-BT, at low estimated concentrations
- $V_O^{\bullet\bullet}$ can be annealed away for long lifetime
- 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 may lead to predominant ionic conductivity in BZT-BT in typical application temperatures (atypical of other capacitor materials)

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