Aging and fatigue in ferroelectrics: experimental results and current understanding

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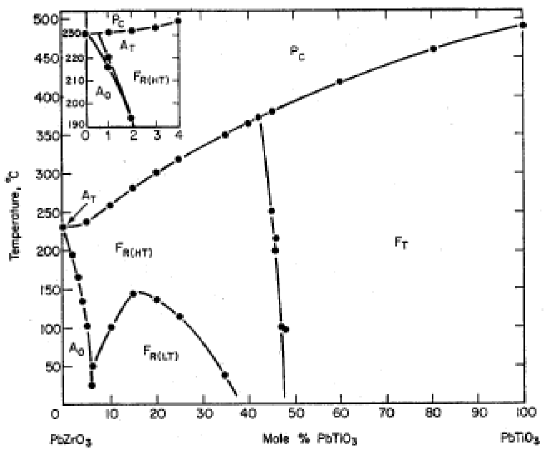
Final Symposium of SFB 595, Sellin, September 2014

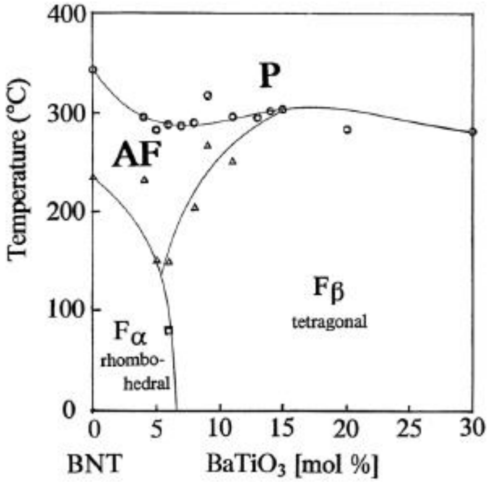
Layout

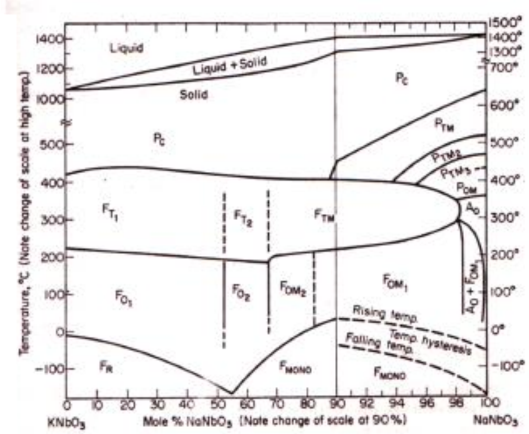
- State-of-the-art at the beginning of the collaborative research (2003)
- Experimental results
- Modelling
- Actual understanding

Material systems studied

PZT **BNT-BT** **KNN**







(a) $Pb[Zr_{1-x}Ti_x]O_3$ (PZT) (from Ref. [6]) (b) $[Bi_{1/2}Na_{1/2}]TiO_3-BaTiO_3$ (BNT-BT) (from Ref. [17])) $[K_x,Na_{1-x}]NbO_3$ (KNN) (from Ref. [6])

This talk is about bulk PZT and BT

Historical notes

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The earliest observations of aging (degradation at equilibrium conditions)

Bogoroditskii & Verbitskaya (1952)
Novosiltsev, Khodakov & Shulman (1952)
Kambe (1953)

First concepts of aging

Mason (1955)
(Slow temperature-induced motion of domain walls)
Plessner (1956)
(A wide distribution of activation energies, reflecting the random character of obstacles to domain wall motion in a ceramic, yields the log(t) law)
Takahashi (1970)
(Space charge effect)
Lambeck & Jonker (1978)
(Re-orientation of polar defects)

The earliest observations of fatigue (gradual degradation during cycling loading)

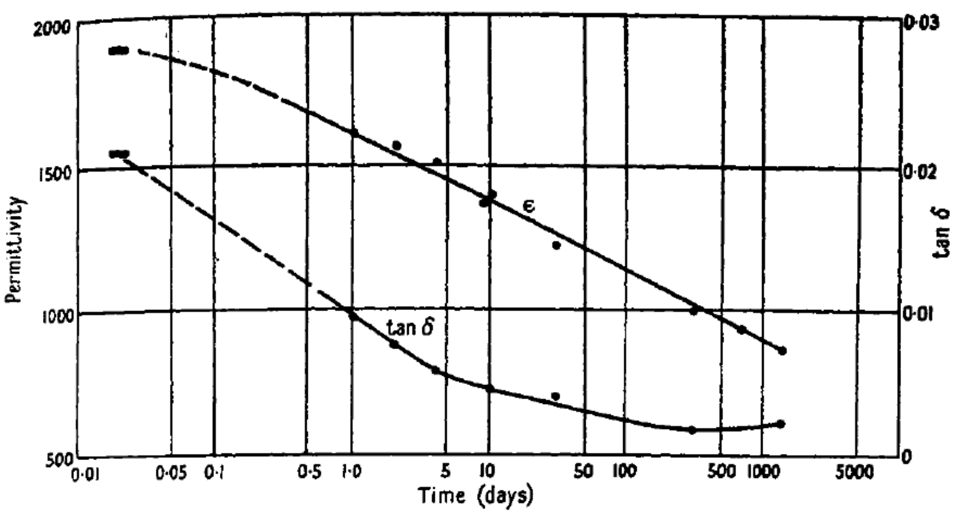
Merz & Anderson (1955)
Anderson et al. (1955)
Taylor (1967)

First concepts of fatigue

Yoo & Desu (1992)
(Defect migration to electrodes)
Brennan (1993)
(Defect accumulation and DW pinning)
Dawber & Scott (2000)
(Defect re-arrangement)

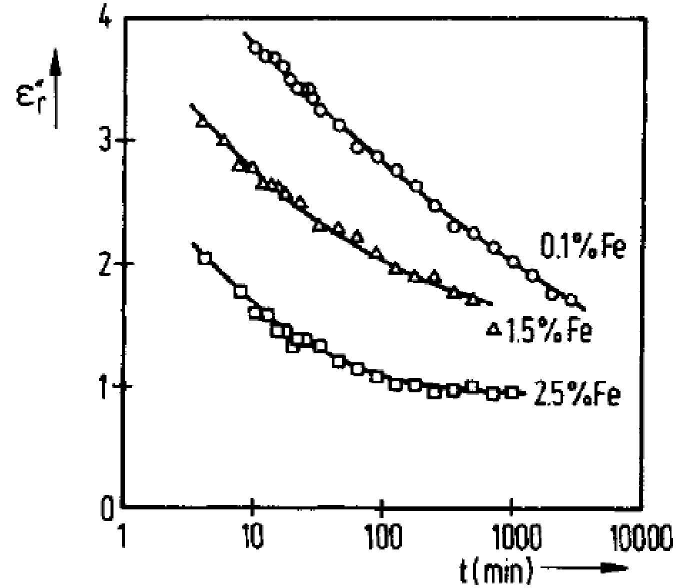
Classical experiments on aging: degradation of permittivity

$(Ba_{0.9}Sr_{0.1})TiO_3$ + 0.5% MgF_2



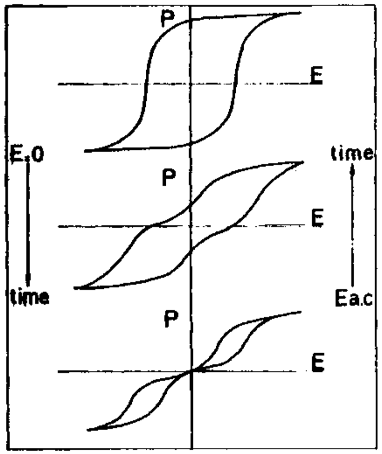
Plessner, Proc. Phys. Soc. Lon. B **69**, 1261 (1956)

$Pb(Zr_{58},Ti_{42})_{1-x}Fe_xO3$

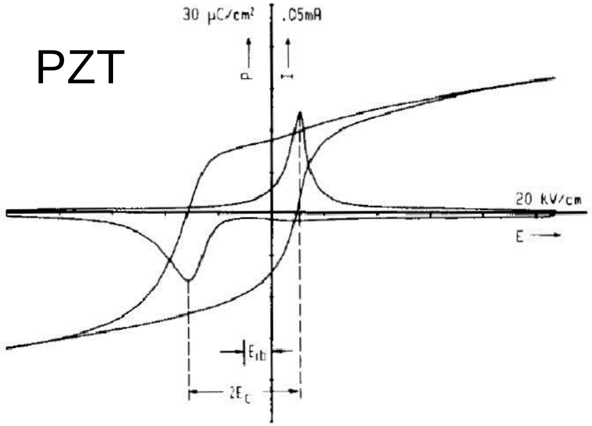


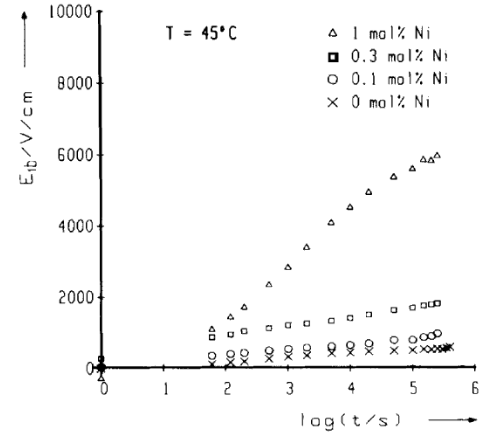
Herbiet et al., Ferroelectrics **76**, 319 (1987)

Classical experiments on aging: internal bias field

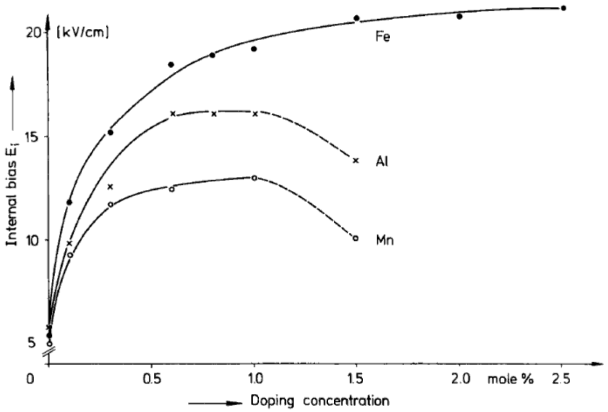


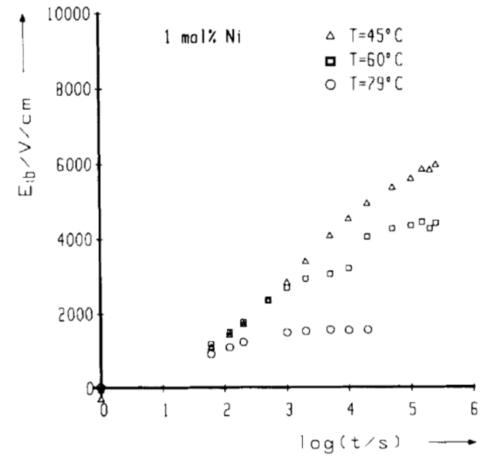
PZT





BT





Carl & Härdtl, Ferroelectrics **76**, 319 (1978)

Arlt & Neumann, Ferroelectrics **87**, 109 (1988)

Classical experiments on aging: de-aging

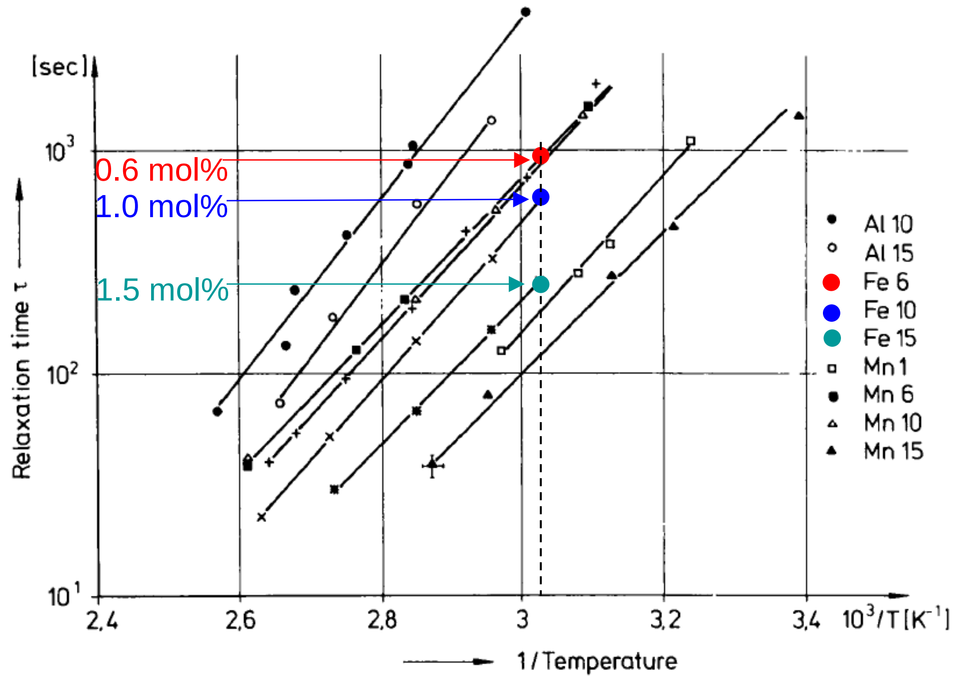


FIGURE 11 Temperature dependence of the relaxation time, τ, of $Pb(Ti_{0.42}Zr_{0.58})O_3$ specimens doped with Mn, Al, and Fe.

E_A=0.6-0.7 eV for (Mn and Fe) and 0.8 eV for Al in PZT

Carl & Härdtl, Ferroelectrics **76**, 319 (1978)

Recent experiments on aging and de-aging

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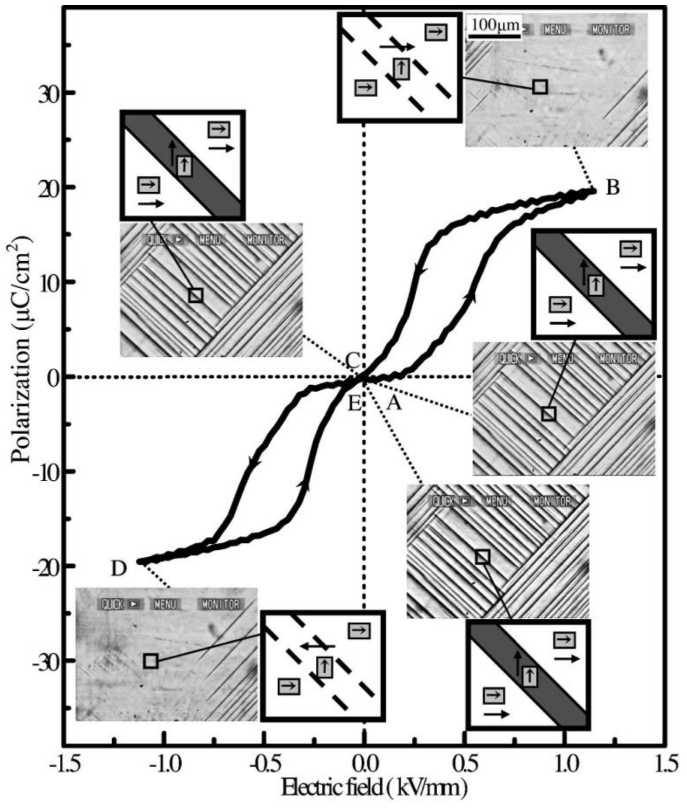
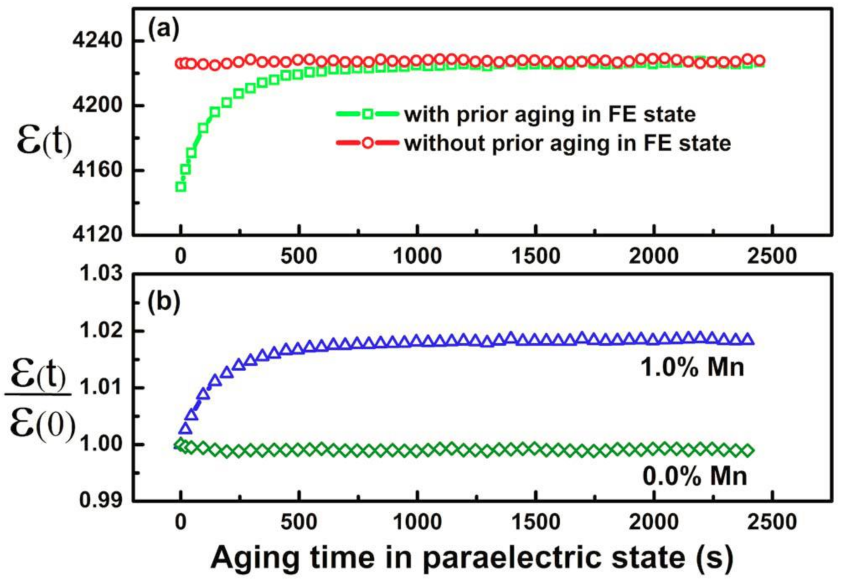
Domain structure evolution during poling



Permittivity evolution during heat treatment



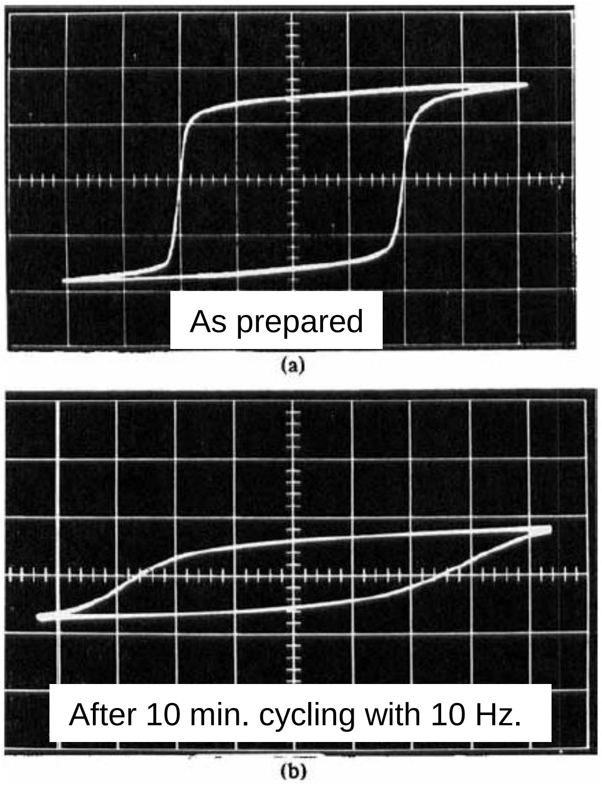
E_A=0.43 eV (for Mn)

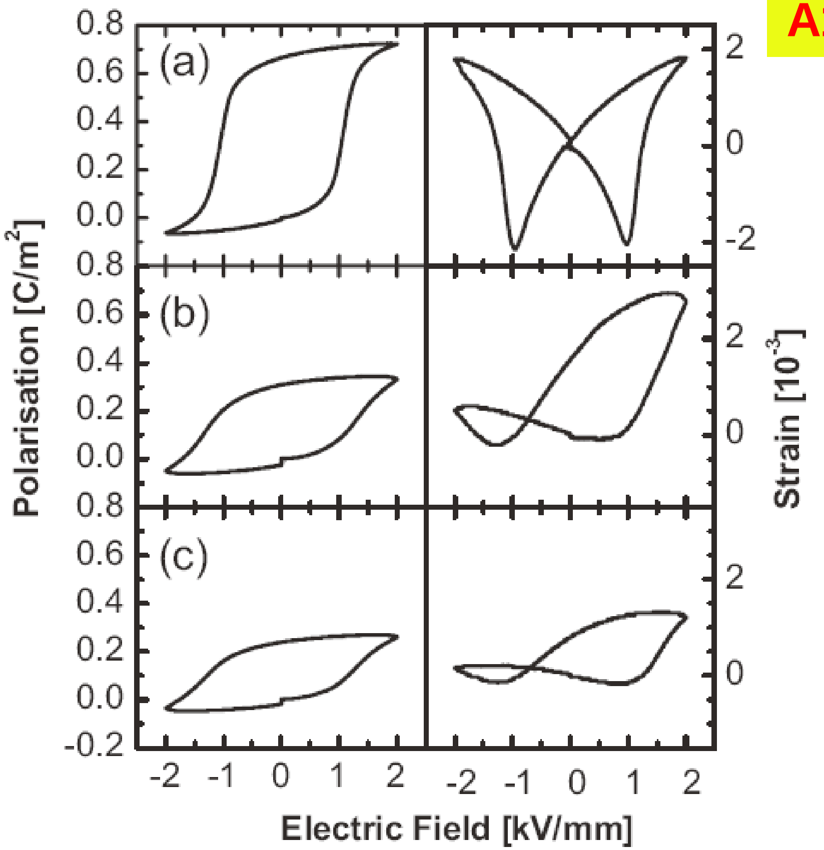
Zhang and Ren, PRB 71 (2005) 174108

Zhou et al., J. Phys.: Condens. Matter **25**, 435901 (2013)

Typical fatigue behaviour

A1,D1





Carl, Ferroelectrics **9**, 23 (1975)

Lupascu & Rödel, Adv. Eng. Mat. **7**, 882 (2005)

Strategy of fatigue studies

A1,D1

Different Regimes

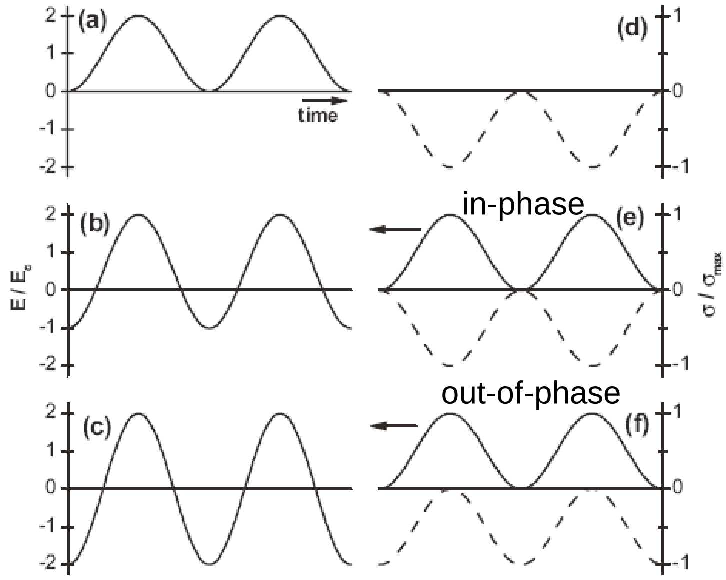
DC electric load

Unipolar electric load

Sesquipolar electric load

Bipolar electric load

Electromechanic load



Particular factors

Field amplitude, frequency and cycle number

Influence of temperature

Role of electrodes

Doping and defects

Lupascu and Rödel, Adv. Eng. Mat. **7**, 882 (2005)

Unipolar, bipolar, sesquipolar and DC conditions of electric load

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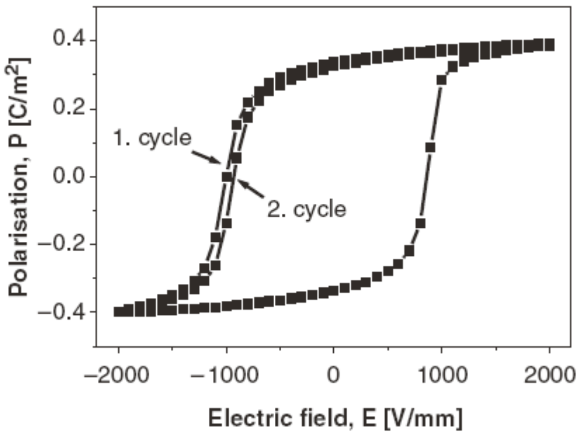
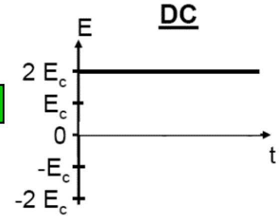
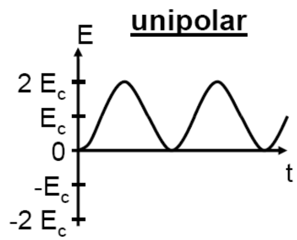
After a DC load of 2 kV/mm for 264 h

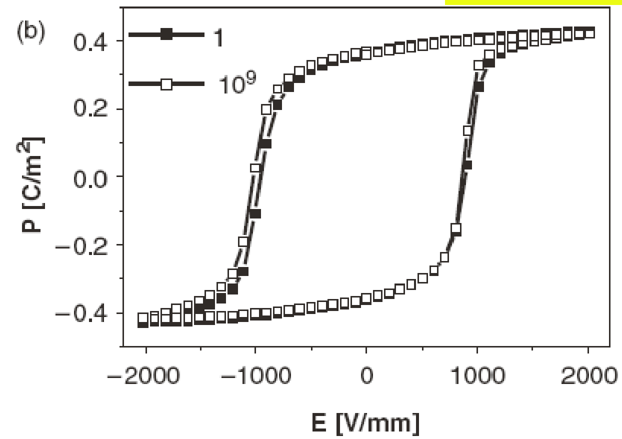


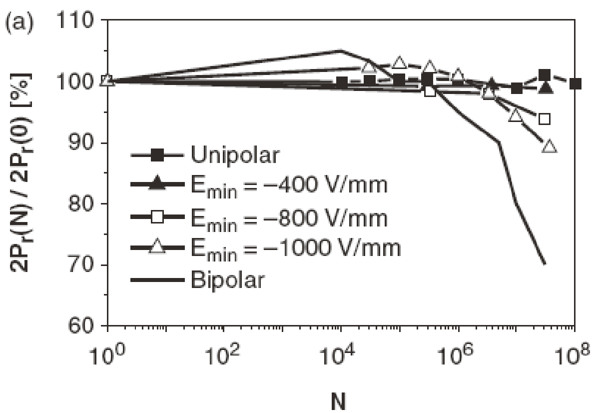


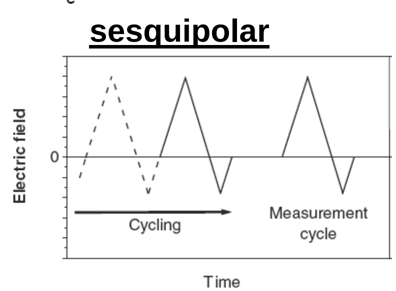


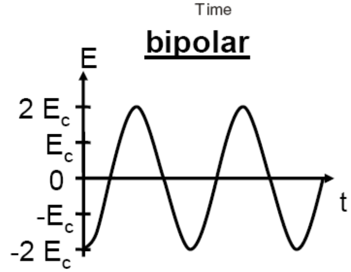
After 10^9 unipolar cycles

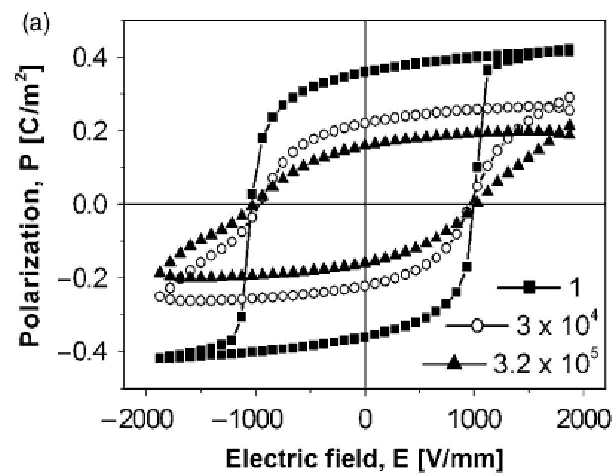
A1,A2,D1







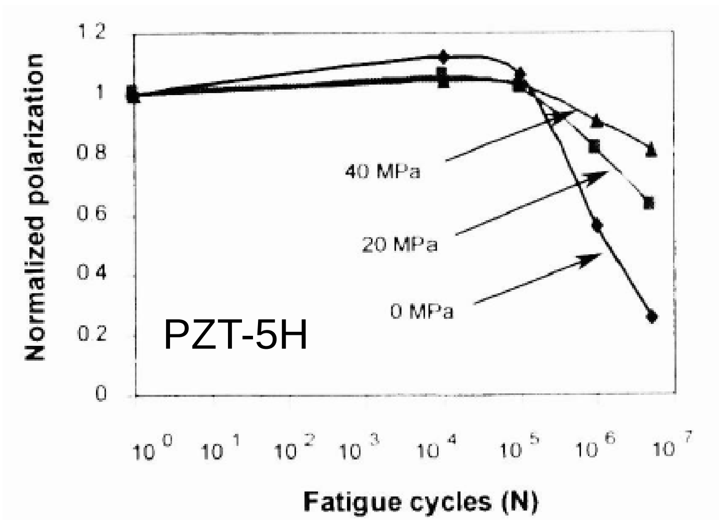




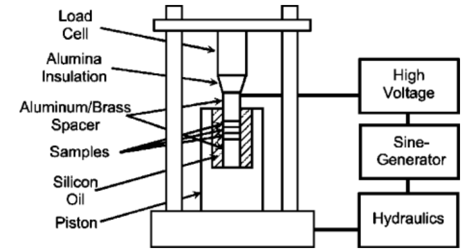
Balke et al. JACS **90** (2007) 1081; 1088; 3869

Cycling with electromechanic loading

D1

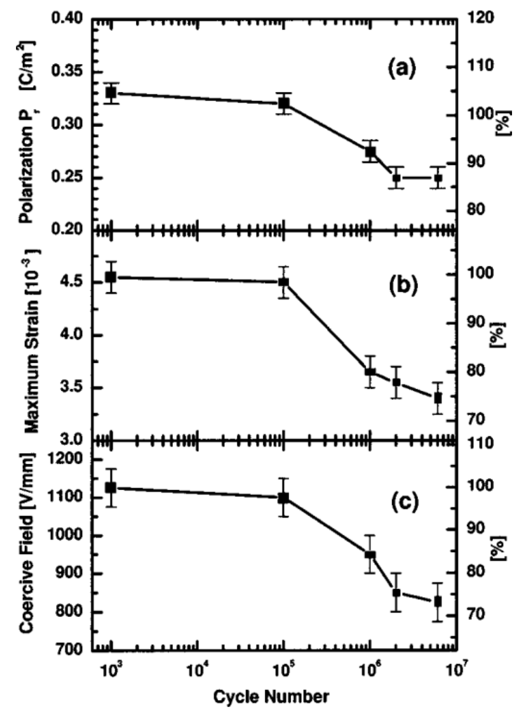


Beneficial effect of a fixed mechanical preload



Detrimental effect of the out-of-phase cycling mechanical loading

Wang & Carman, Smart Structures and Integrated Systems (1998) 210–221



Lupascu et al., JAP **93**, 5551 (2003)

Effects of the field amplitude, frequency and cycle number

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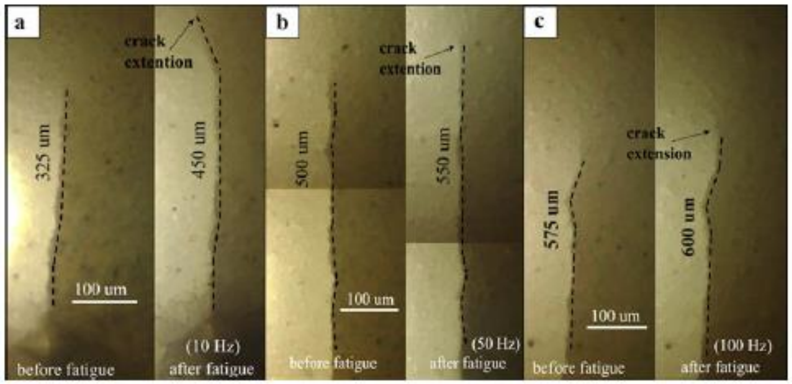
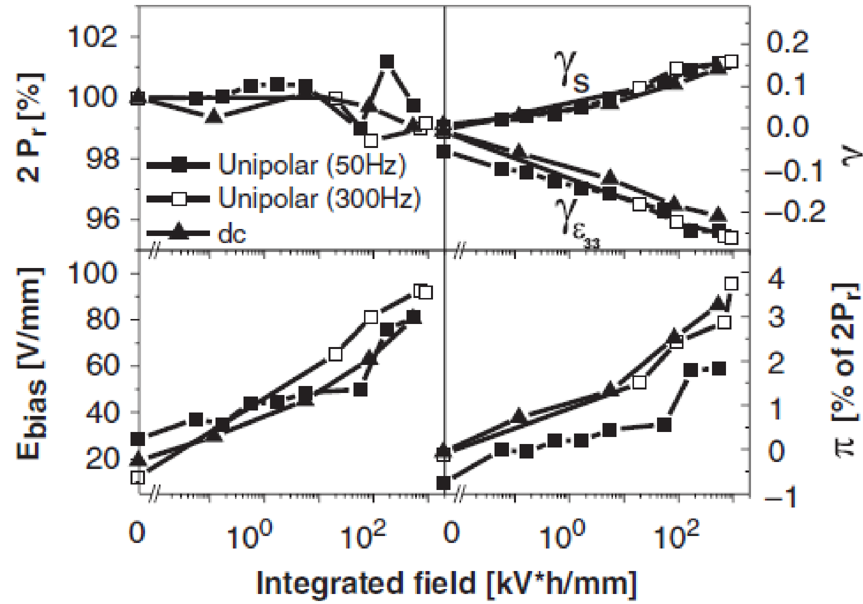
D1

Increasing frequency reduces crack growth in soft PZT

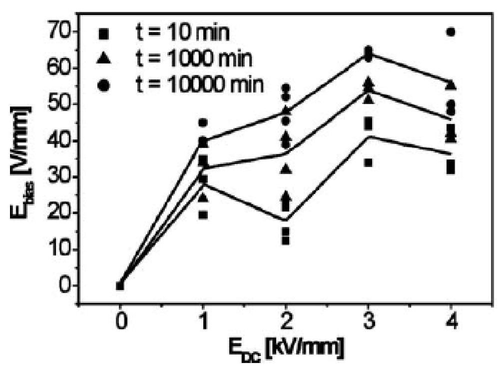


Pojprapai et al., Acta Mat. 57 (2009) 3932

Unipolar fatigue in PIC 151



Balke et al. JACS **90**, 1081 (2007)



Saturation at E_{DC} > 2Ec

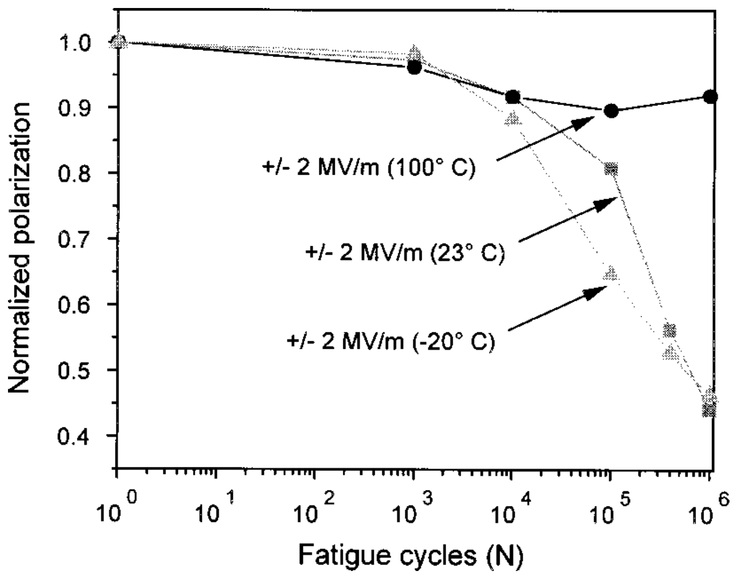
Balke et al. JAP **105**, 104105 (2009)

An increasing cycling field amplitude above the coercive field leads to stronger degradation of both dielectric and piezoelectric parameters of PZT-5H (Wang et al., JAP **83,** 5342 (1998))

Temperature influence on fatigue

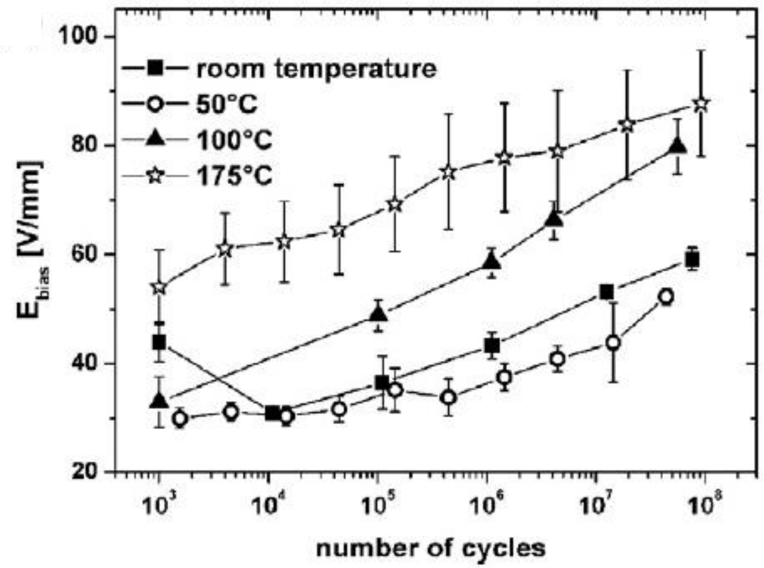
B3,D1

Development of polarization in PZT-5H



Wang et al., JAP **83** , 5342 (1998)

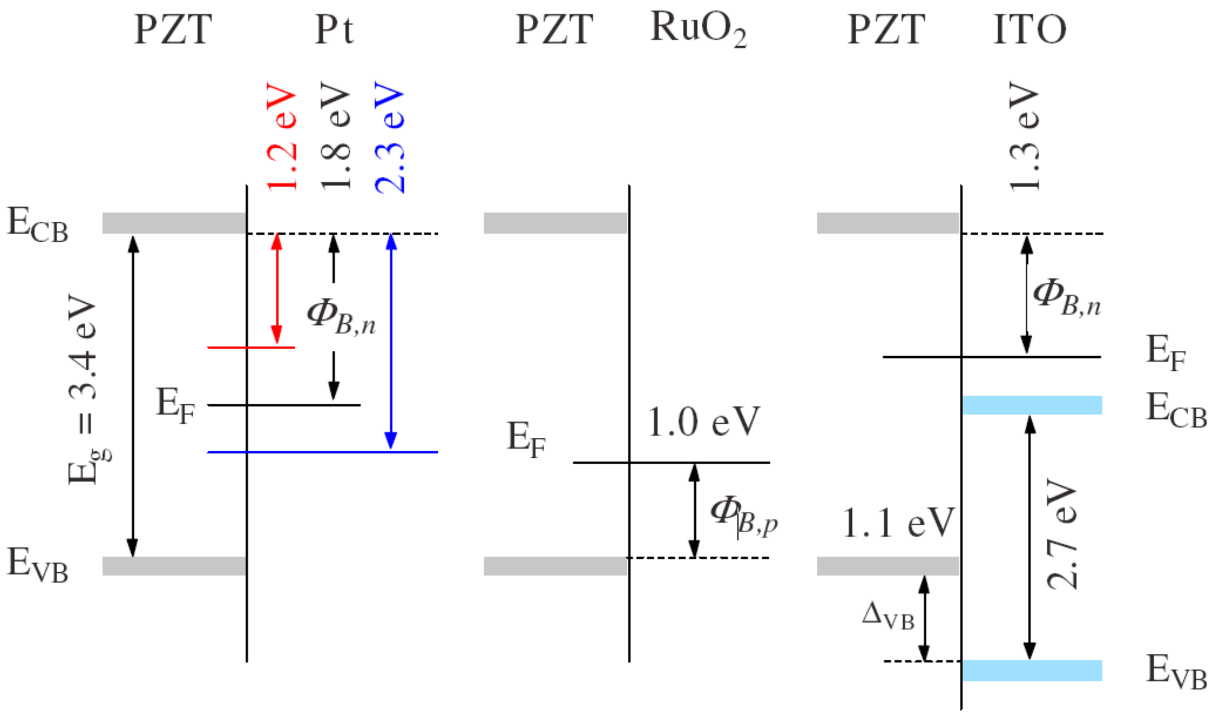
Development of bias field in PIC 151



Glaum et al., Acta Mat. **59**, 6083 (2011)

Impact of electrodes: injection barriers from X-ray photoemission spectra

B7,D3

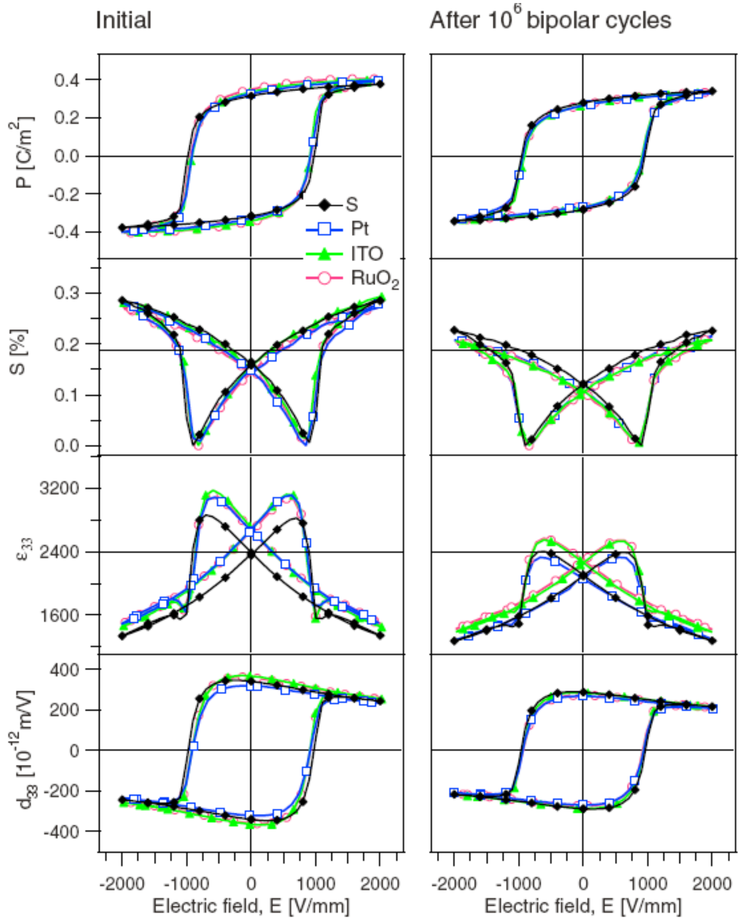


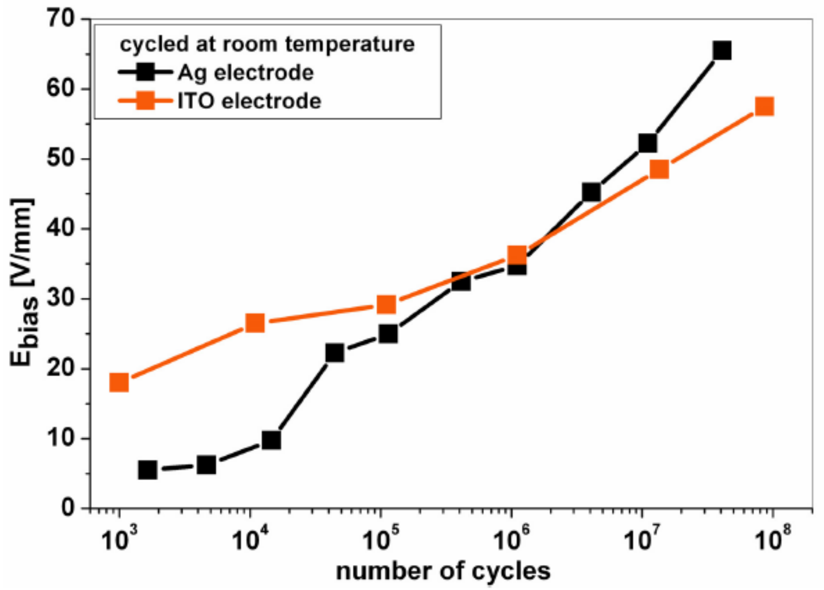
- Barrier heights strongly depend on electrode material
- Barrier heights with Pt vary by ~1eV depending on pO_2

Chen et al. J. Phys. D: Appl. Phys. **42** (2009) 215302; **43** (2010) 295301; JAP **108** (2010) 104106

Fatigue in PIC 151 with Pt, RuO_2, ITO and Ag electrodes

B7,D1





No crucial difference in polarization and (bipolar) fatigue with different electrodes in contrast to thin films

Chen et al. JAP **108**, 104106 (2010)

Experimental verification of fatigue models by different methods

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Anticipated origins of fatigue can be separated in two main groups:

- Occurrence of microstructural changes such as crack initiation or element migration (irreversible, meso- to macroscopic)
- Alteration of domain wall motion due to polar defect alignment and/or charge carrier agglomeration (reversible, micro- to mesoscopic)

Methods implemented:

Optical microscopy, high-resolution synchrotron radiation, EDX, HRSEM, TEM, EPR, NMR, pulse electric measuremenets etc.

Fatigue of the near electrode region in PZT

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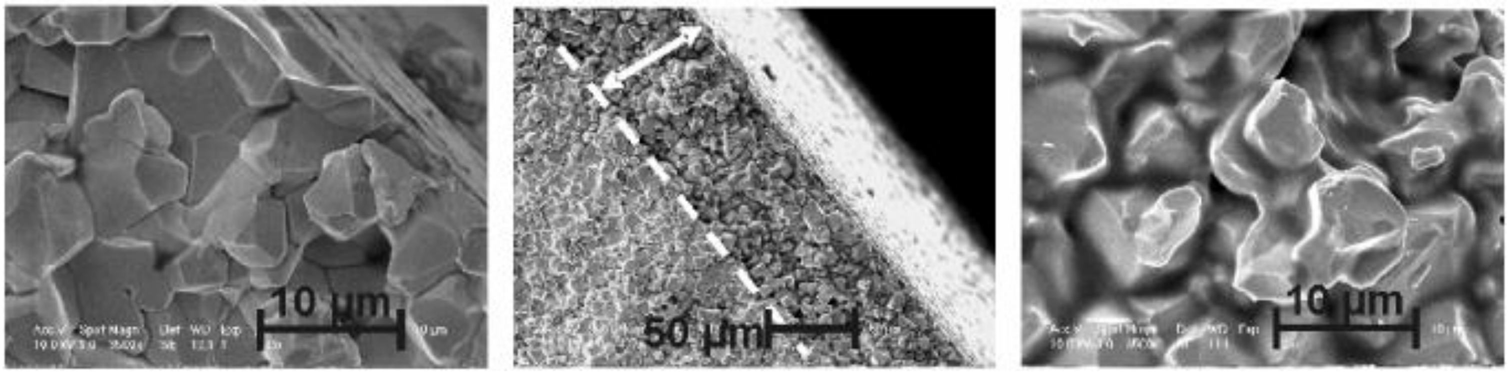
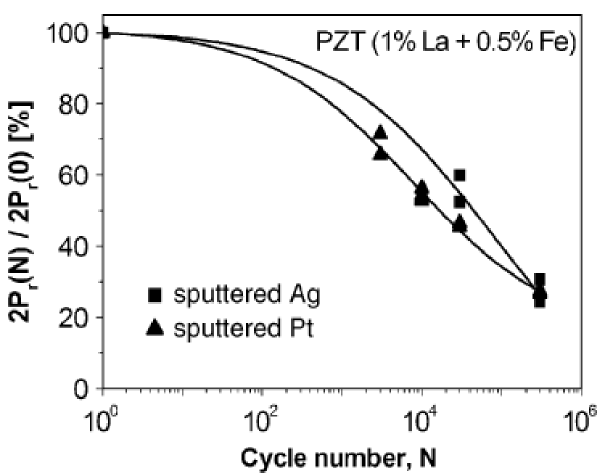
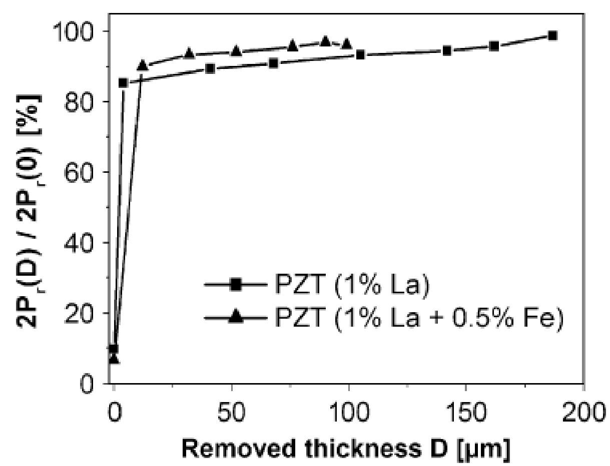
A2,D1

SEM images before and after $3x10^5$ bipolar cycles

(a) (b) (c)







Balke et al. JACS **90** (2007) 1081; 1088; 3869

Structural changes during electrical loading by using in-situ high resolution synchrotron radiation

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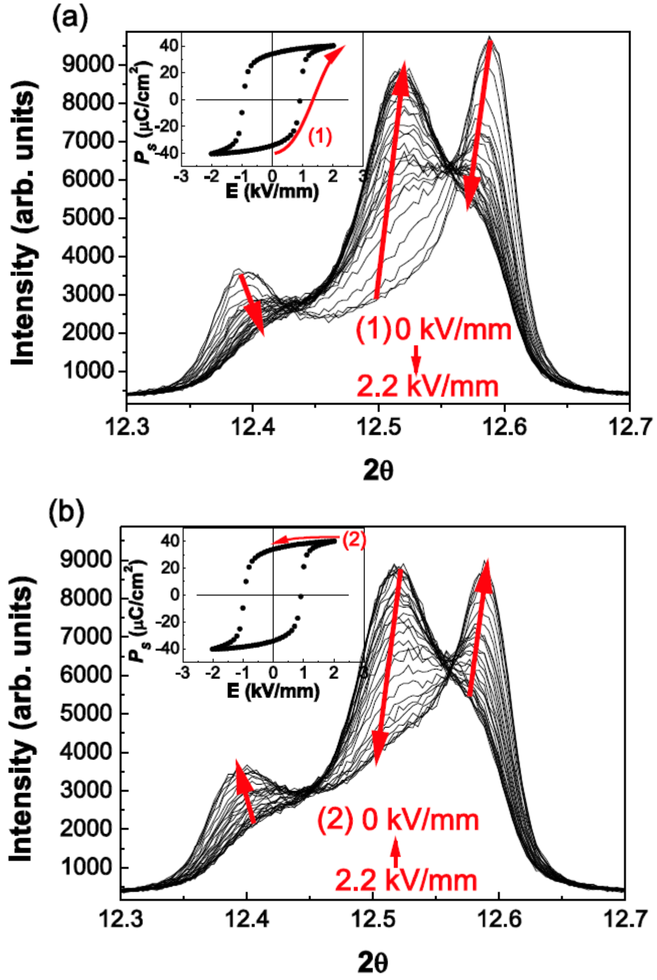
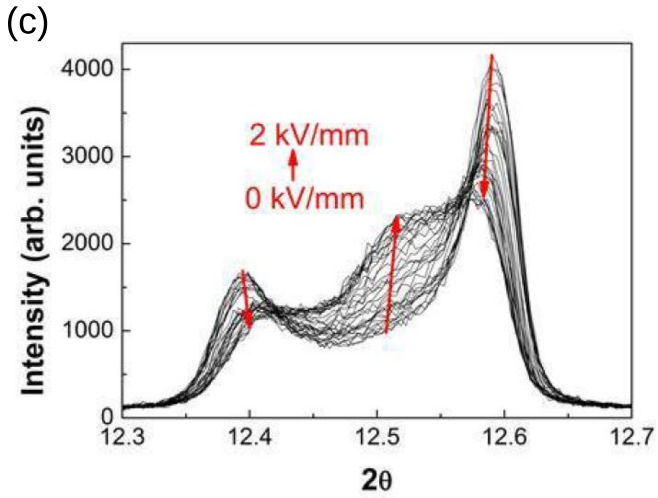
B3,T2



Reversable switching from tetragonal to monoclinic phase in PZT at MPB

Reduced phase transformation after 10^7 bipolar cycles



Hinterstein et al. PRL **107**, 077602 (2011)

Polarization switching in fatigued PZT ceramics

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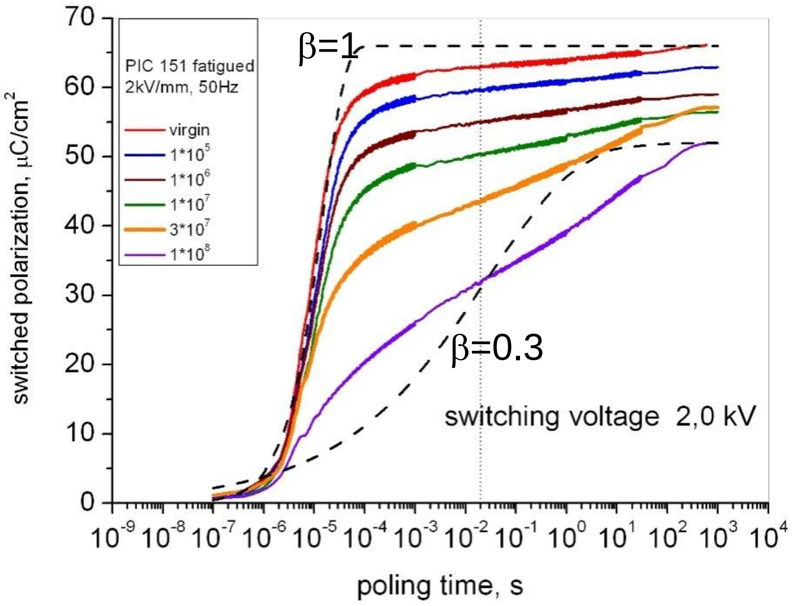
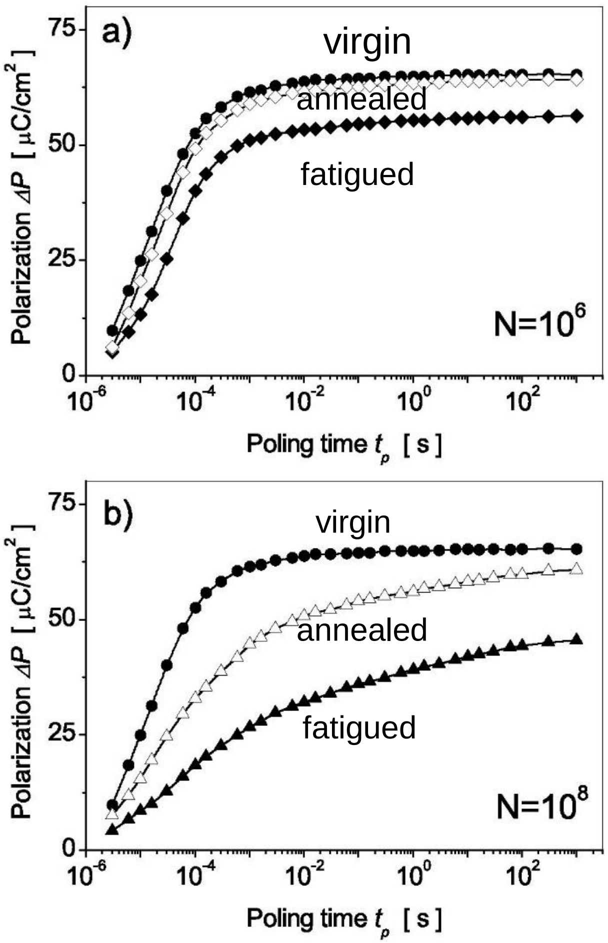
PIC 151 ceramic (virgin and fatigued)

Annealing experiment **B7,C5,D1**



Zhukov et al., JAP **108**, 014105 (2010)



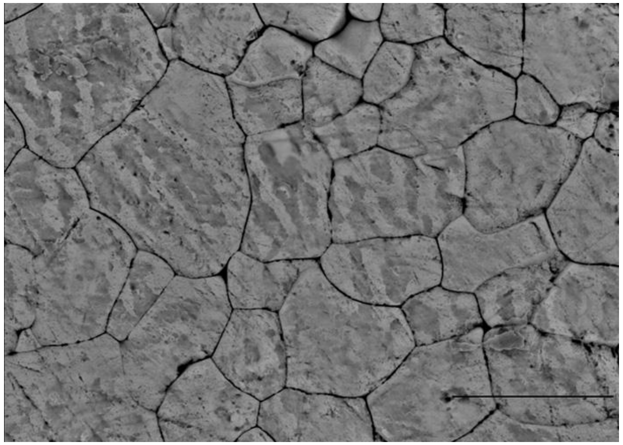
Zhukov et al., PRB **82**, 014109 (2010)

Crack formation in heavily doped PZT

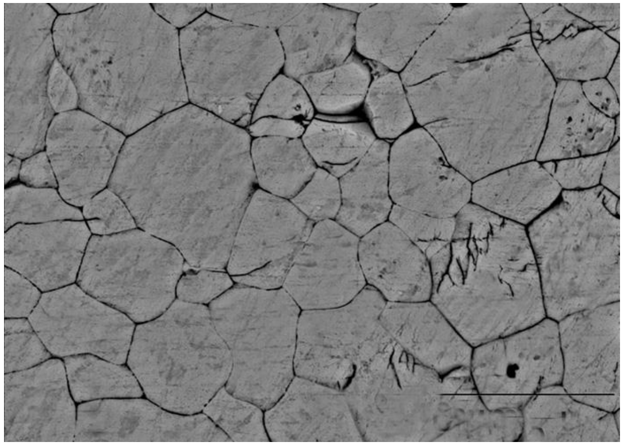
B7,C5,D1

SEM

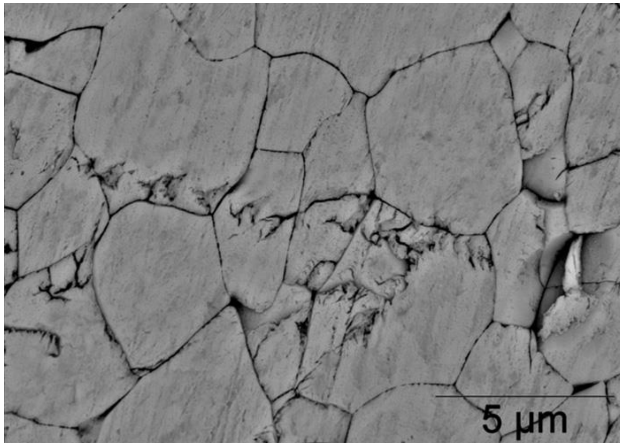
fresh ceramic



10^7 cycles



10^8 cycles



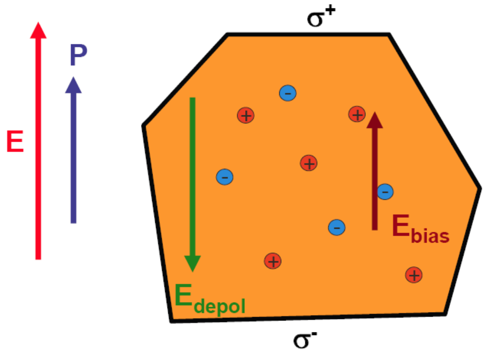
Zhukov et al. JAP **108**, 014105 (2010)

Ionic and electronic processes behind reversible fatigue and aging

C1,C5,D1

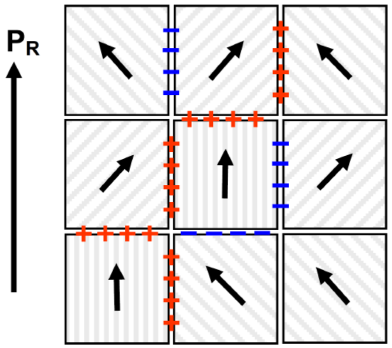
Charge accumulation in grain boundaries

during fatigue



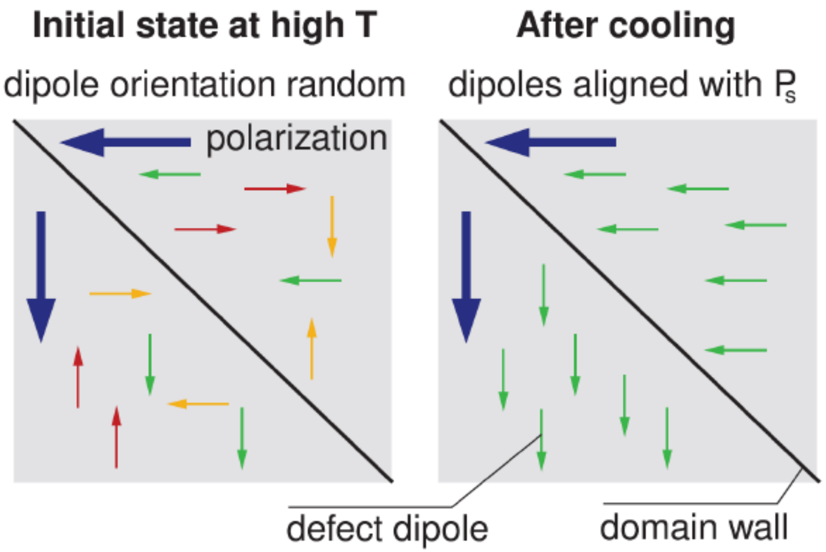
Balke et al.,
JAP **105** (2009) 104105

during aging in poled state



Genenko et al.,
PRB **80**, 224109 (2009)

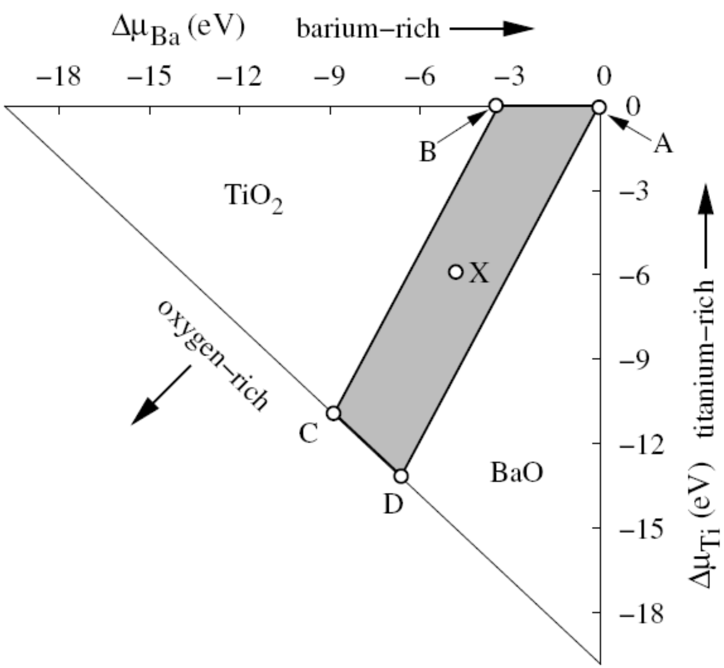
Dipole defects re-orientation

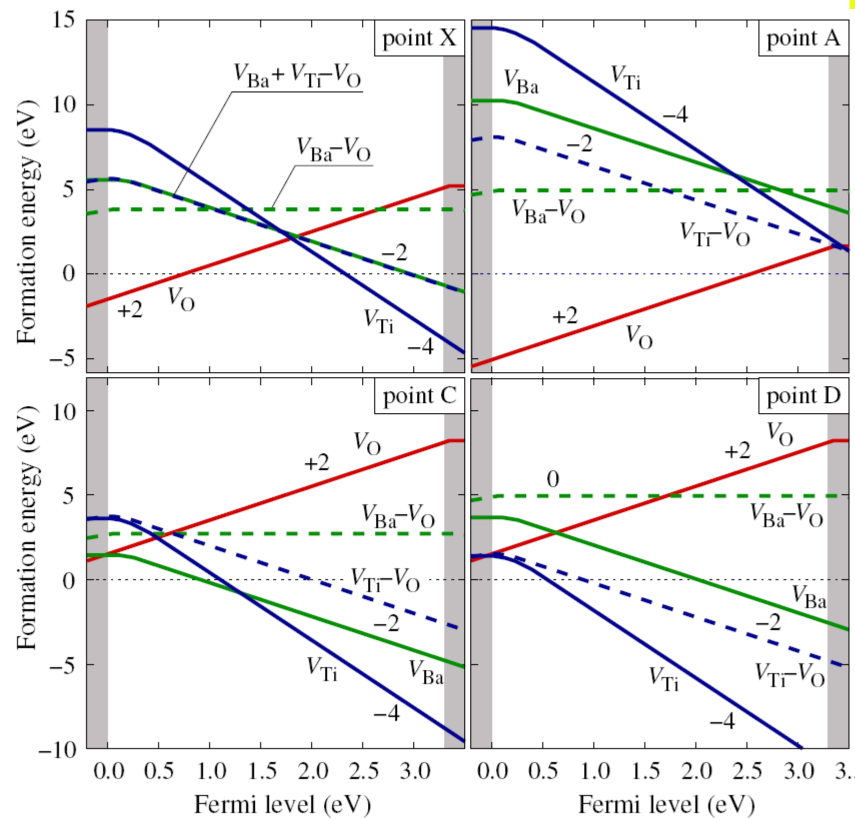


Erhart et al., PRB **88**, 0124107 (2013)

Defect formation energies in $BaTiO_3$ by DFT

C1





Erhart & Albe, J. Appl. Phys. **104**, 044315 (2008)

Oxygen tracer (^{18}O) diffusion in $PbZr_{0.4}Ti_{0.6}O_3$

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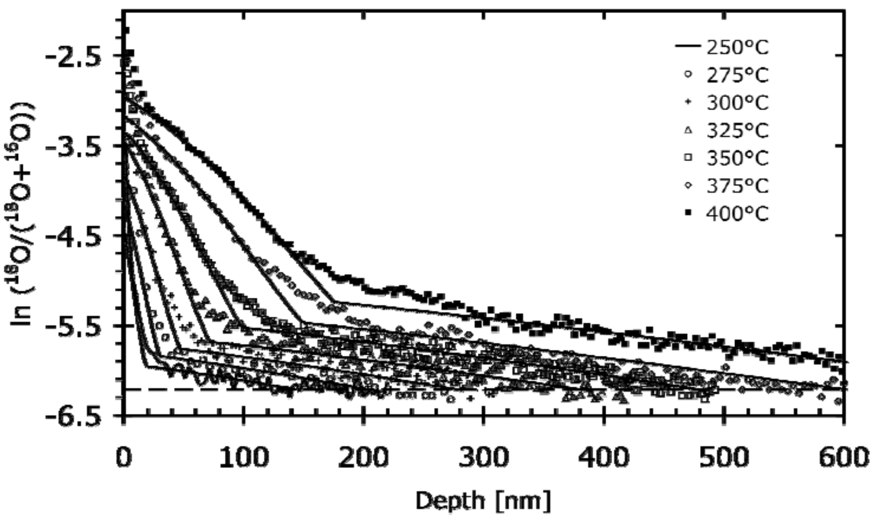
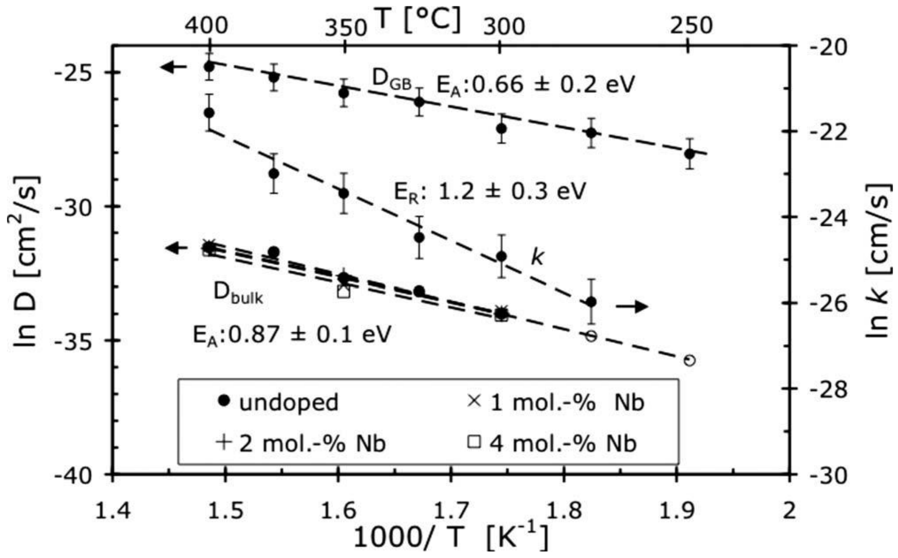
B2

Isotope ratio depth profiles from SIMS





Activation barriers for oxygen motion
in bulk E_A~1.2 eV
in grain boundaries E_A ~0.66 eV

Gottschalk et al., JAP **104**, 114106 (2008)

Defect dipole formation, position and orientation from ESR and DFT

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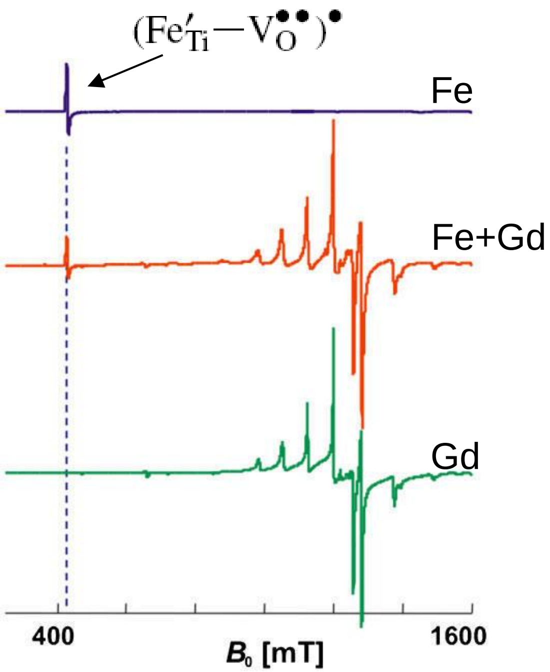
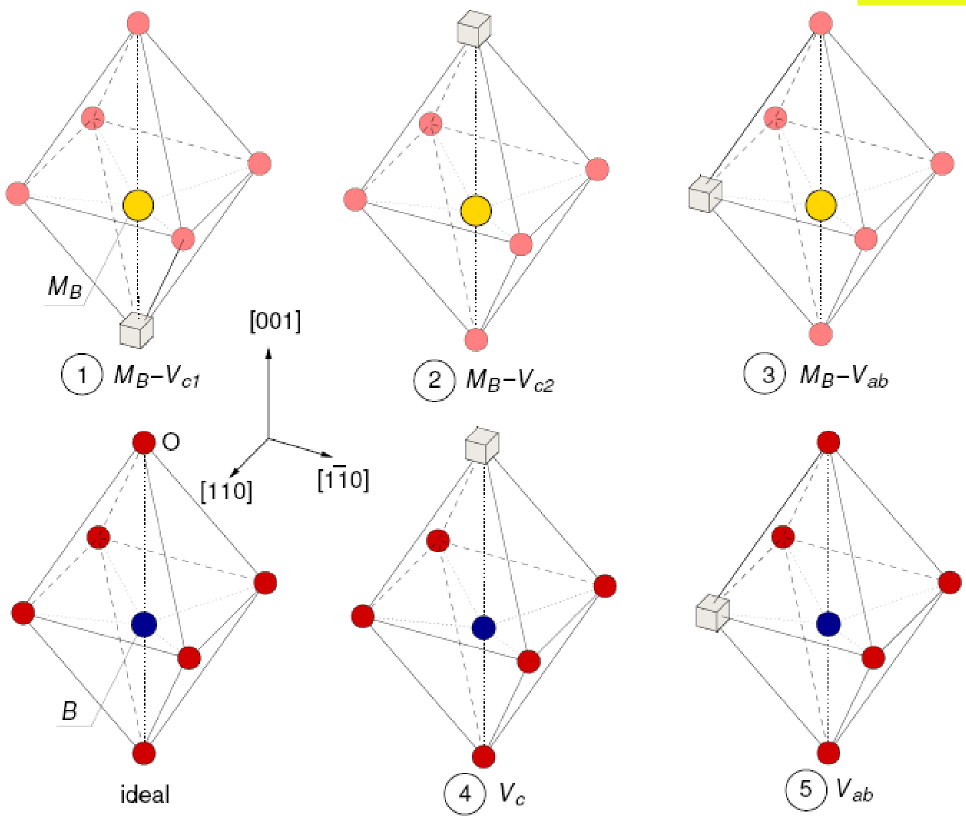
A2,B1,C1

Differently doped $PbTiO_3$



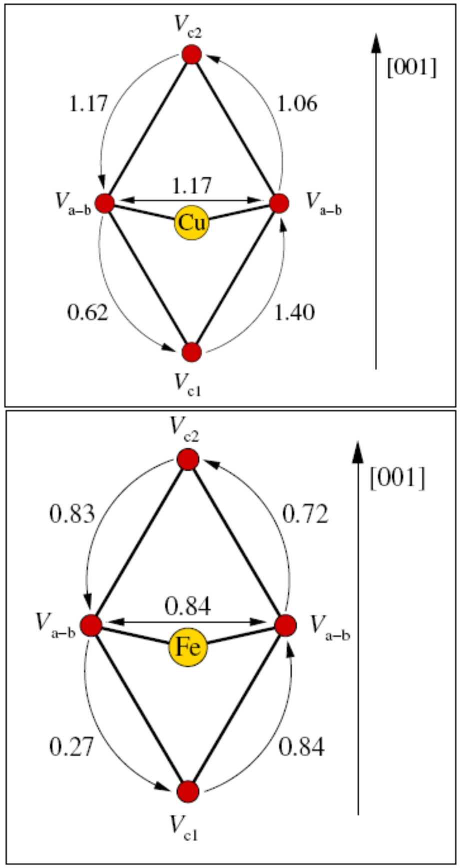


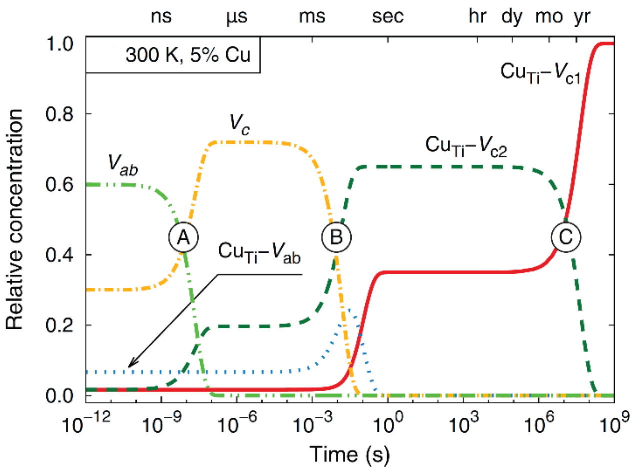
Eichel et al., JAP **95**, 8092 (2004)
Jakes et al., APL **98**, 072907 (2011)

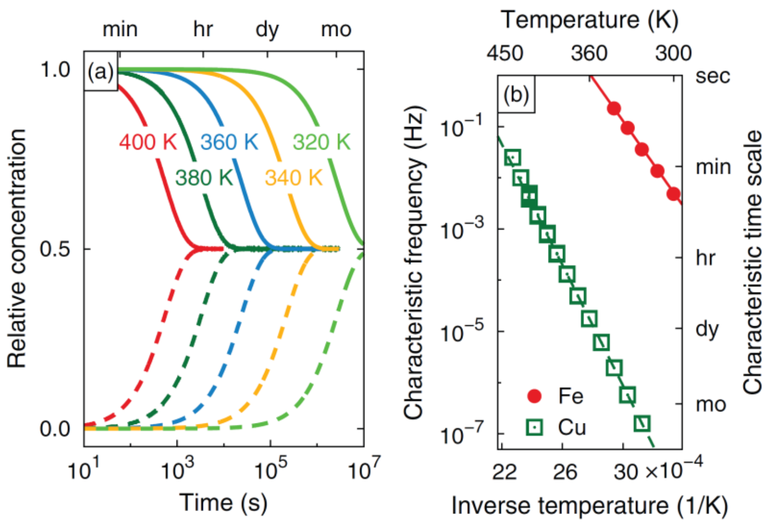
Erhart et al., PRB **76**, 174116 (2007); **88**, 024107 (2013)

DFT analysis of defect dipole switching barriers and alignment kinetics in doped PT

C1







Erhart et al., PRB **88**, 024107 (2013)

Drift-diffusion model of aging in unpoled polycrystalline ferroelectrics I

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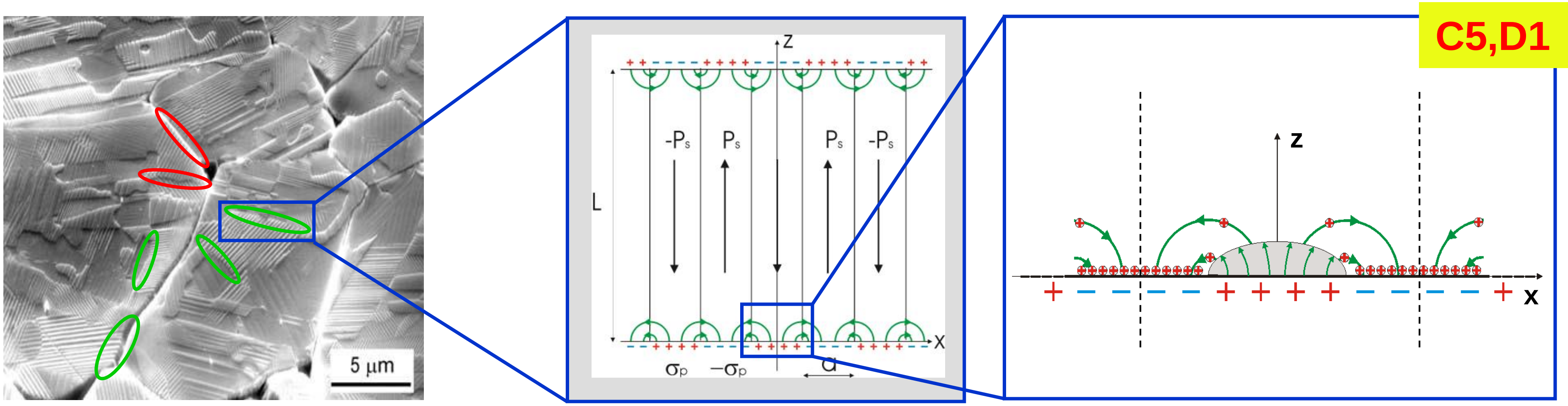

Main assumptions of the model

- Presence of local depolarization fields at some domain faces
- Existence of sufficient amount of mobile charge carriers (presumably, oxygen vacancies) in the bulk material
- Stability of the domain structure during the charge migration

Basic equations

$$\frac{\partial c}{\partial t} = -\nabla\left(\mu c \mathbf{F}\right) + D\Delta c$$

$$\nabla \mathbf{F} = \frac{q_f}{\varepsilon_r \varepsilon_0}\left(c - c_0\right)$$

Low doping limit: Genenko & Lupascu, PRB **75**, 184107 (2007); Genenko et al.Ferroelctrics **370**, 196 (2008)

Drift-diffusion model of aging in unpoled polycrystalline ferroelectrics II

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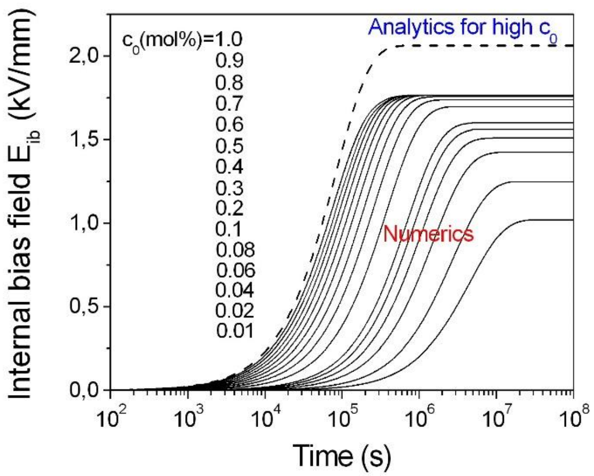
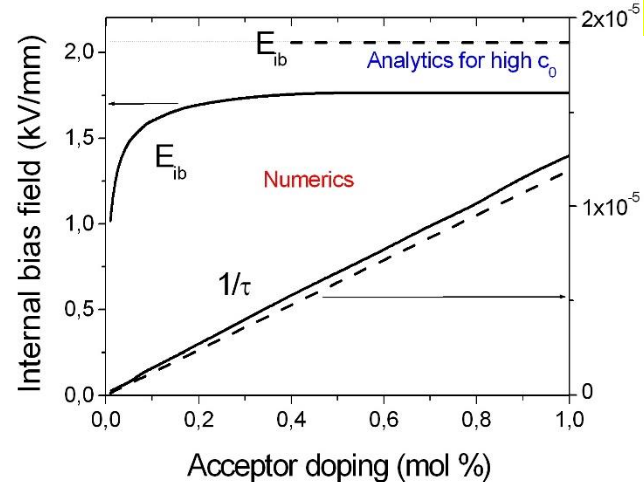
C5



Numerical results for arbitrary doping



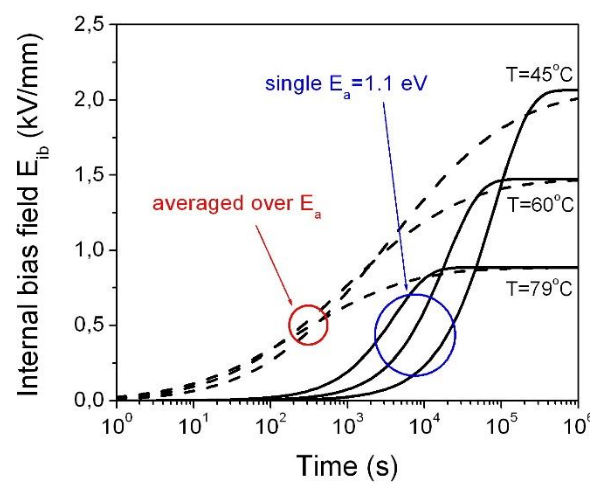
Analytical results For c_0>0.4 mol%

Aging time:

$$\tau_r = \varepsilon_0 \left(\varepsilon_f + \varepsilon_d\right) / q_f \mu c_0$$

Internal bias field:

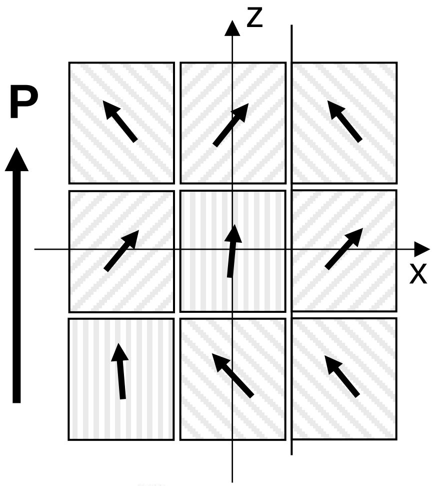
$$E_{ib}(t) = \frac{0.85}{\pi} \frac{a}{L} \frac{P_s}{\varepsilon_0 \varepsilon_f} [1 - \exp(-t/\tau_r)]$$



Arbitrary doping: Genenko, PRB **78**, 214103 (2008)

Drift-diffusion model of aging in poled polycrystalline (PZT) ferroelectrics

A2,C5,D1

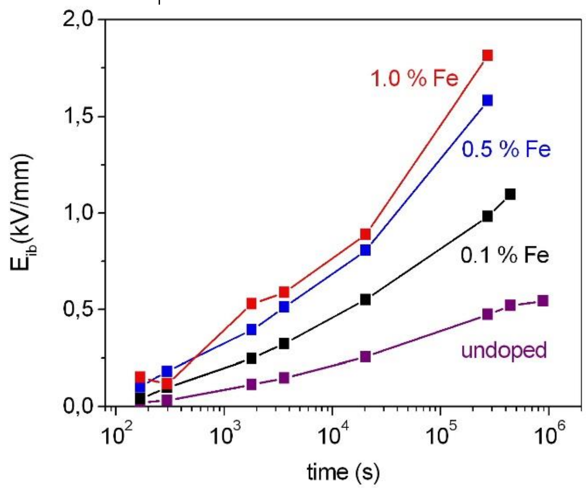


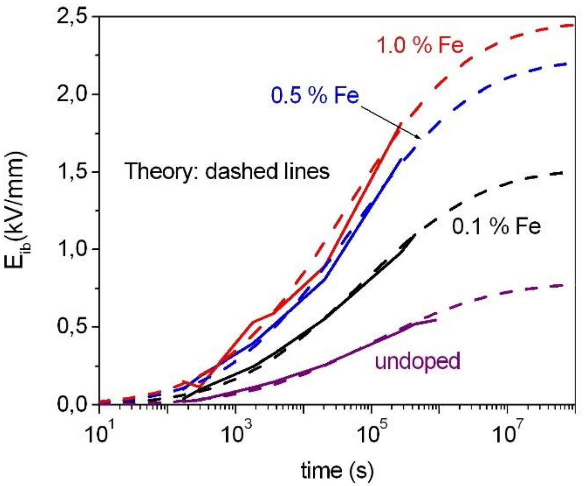
Main assumptions of the model

- Presence of local charges and, consequently, depolarization fields due to mismatch of polarizations in neighbor grains
- Existence of mobile charge carriers (presumably, oxygen vacancies) in the bulk material

$$\sqrt{\left\langle \Delta \mathbf{E}_d^2 \right\rangle} \cong \frac{3P_s}{4\pi\varepsilon_0\varepsilon_f}$$

$$E_{ib}(t) \cong \frac{2.6}{4\pi}\frac{P_s}{\varepsilon_0\varepsilon_f}[1-\exp(-t/\tau_r)]$$

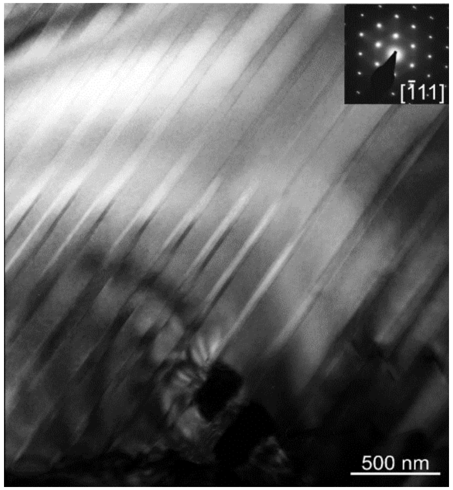




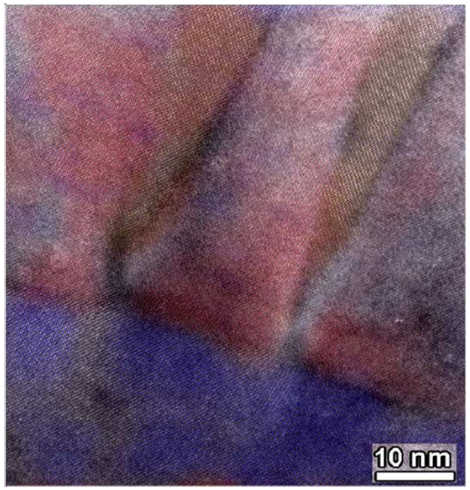
Genenko et al., PRB **80**, 224109 (2009)

Deformation of domains due to agglomeration of charge defects: phase-field modelling

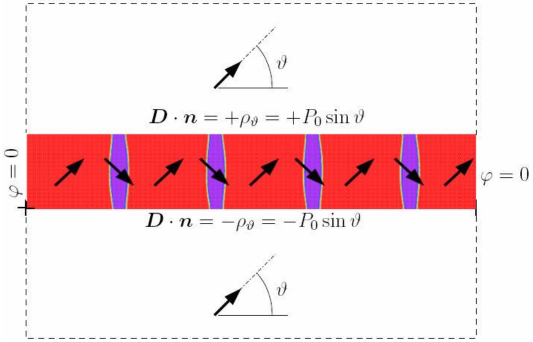
B3,C3

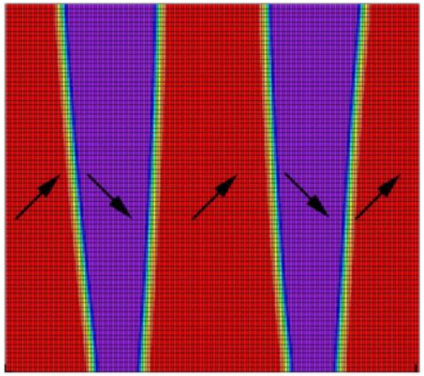


TEM: Schmitt et al.,
JAP **101**, 074107 (2007)

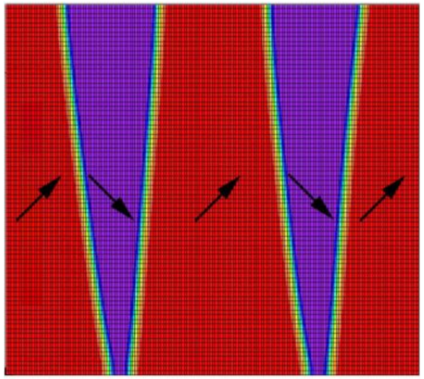


HRTEM: Schmitt et al.,
Comp.Mat.Sci. **81**,123 (2014)





$\vartheta = 12.2°$



$\vartheta = 25.1°$

HRTEM: Schmitt et al., Comp. Mat. Sci. **81**,123 (2014)

Prospects in phase-field modeling: migration of oxygen vacancies in domain structures

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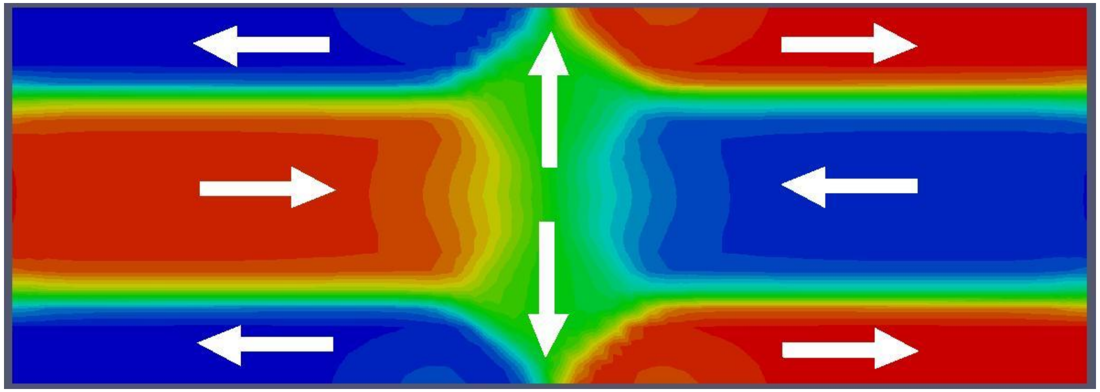
C5,C6,D3



Self-organized stripe domain structure exhibit strong remanent depolarization fields which should further drive mobile charged defects

Zuo et al., JAP **115**, 084110 (2014)

After all: migration of charge defects or re-orientation of defect dipoles?

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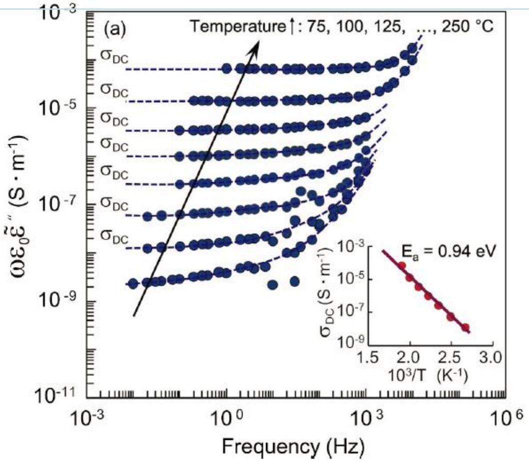
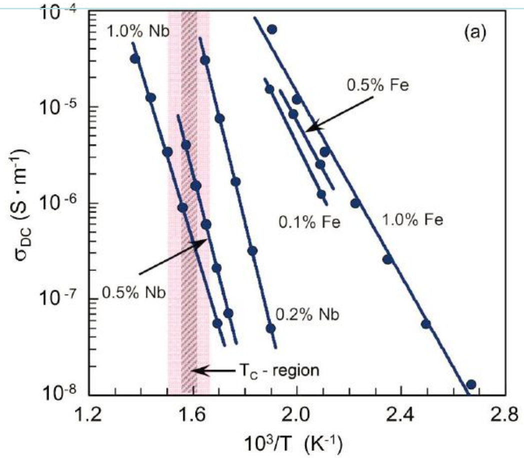
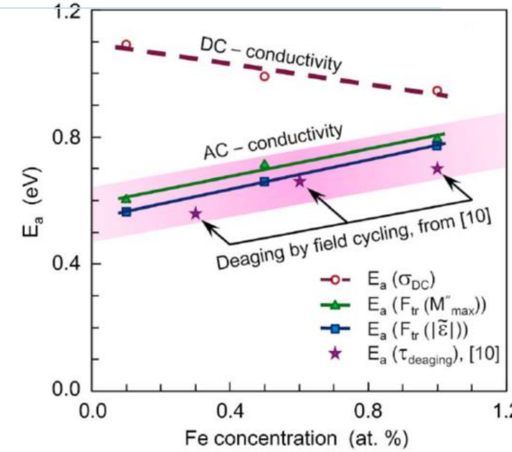
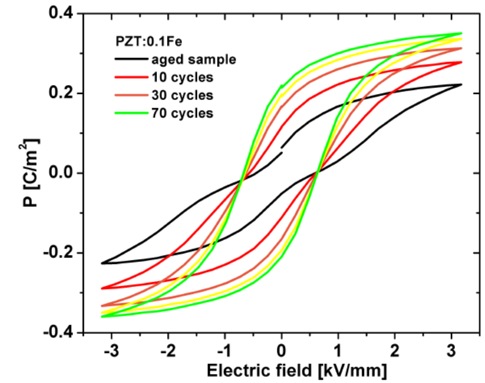






Morozov and Damjanovic, JAP **107**, 034106 (2010)



(DC) in Fe-doped PZT
E_A=0.94-1.2 eV
Long-range migration

(AC) in Fe-doped PZT
E_A=0.55-0.7 eV
Short-range migration

Both mechanisms contribute to aging and fatigue with distinct aging times and activation energies

Glaum et al., JAP **112**, 034103 (2012)

Thank you for your attention!