Electrical Fatigue in Lead-free Piezoelectric Ceramics

UNSW AUSTRALIA

Never Stand Still | Science | School of Materials Science and Engineering

M.J. Hoffman

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UNSW Australia
The University of New South Wales

UNSW AUSTRALIA

We’re different:

- Australia’s leading university focused on **science, technology** and the **professions**
- Founded in 1949. Mission has always been to work closely with industry and business.
- B2B – “*to be a **leading research intensive university** in the **Asia-Pacific region**, focusing on contemporary and social issues through defined strengths in **professional and scientific fields**”*

UNSW AUSTRALIA

UNSW FAST FACTS

Founded
1949
Located in
Sydney

52,614
STUDENT ENROLMENTS

8 FACULTIES

Arts & Social Sciences
Australian School of Business
Built Environment
College of Fine Arts
Engineering
Law
Medicine
Science

13,701
INTERNATIONAL STUDENTS

19,457
COMMENCING ENROLMENTS

1 UNIVERSITY COLLEGE - UNSW Canberra at the Australian Defence Force Academy

5,654
STAFF

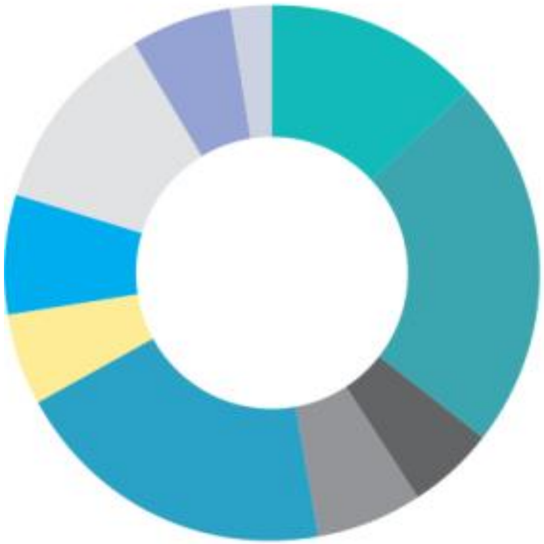
244,861
ALUMNI

52 SCHOOLS

97 AFFILIATED INSTITUTES

8 RESIDENTIAL COLLEGES

UNSW Students by Faculty*



Students by Faculty

7,182	Arts & Social Sciences
12,214	Australian School of Business
2,907	Built Environment
3,497	College of Fine Arts
10,774	Engineering
3,082	Law
3,898	Medicine
6,340	Science
3,273	UNSW Canberra
1,350	Other

* From UNSW Annual Report 2013

RESEARCH

Australian
RANKS

#1 IN RESEARCH OUTPUTS &
#3 IN TOTAL RESEARCH INCOME

GLOBAL

RANKED 52nd IN THE WORLD BY GLOBAL QS RANKINGS
85th TIMES HIGHER ED

EXCHANGE

LAUNCHED EASY ACCESS IP, OFFERING MOST OF OUR INTELLECTUAL PROPERTY TO COMPANIES FOR FREE

BEST

TOP IN FUNDING FOR MEDICAL RESEARCH IN 2014
TOP IN ARC RESEARCH FUNDING IN 2013

HIGHEST

CITATIONS PER PAPER OF ANY AUSTRALIAN UNIVERSITY IN 31 AREAS

QS Discipline Rankings

UNSW 16 Disciplines World Top 50

Materials Science	17
Civil & Structural Engineering	18
Computer Science & Information Systems	29
Electrical & Electronic Engineering	33
Mechanical, Aeronautical & Manufacturing Engineering	37
Chemical Engineering	46
Pharmacology	11
Psychology	15
Economics & Econometrics	45
Law	14

Electrical Fatigue in Lead-free Piezoelectric Ceramics

Mark Hoffman

Never Stand Still | Science | School of Materials Science and Engineering

SFB 595

Deutsche Forschungsgemeinschaft

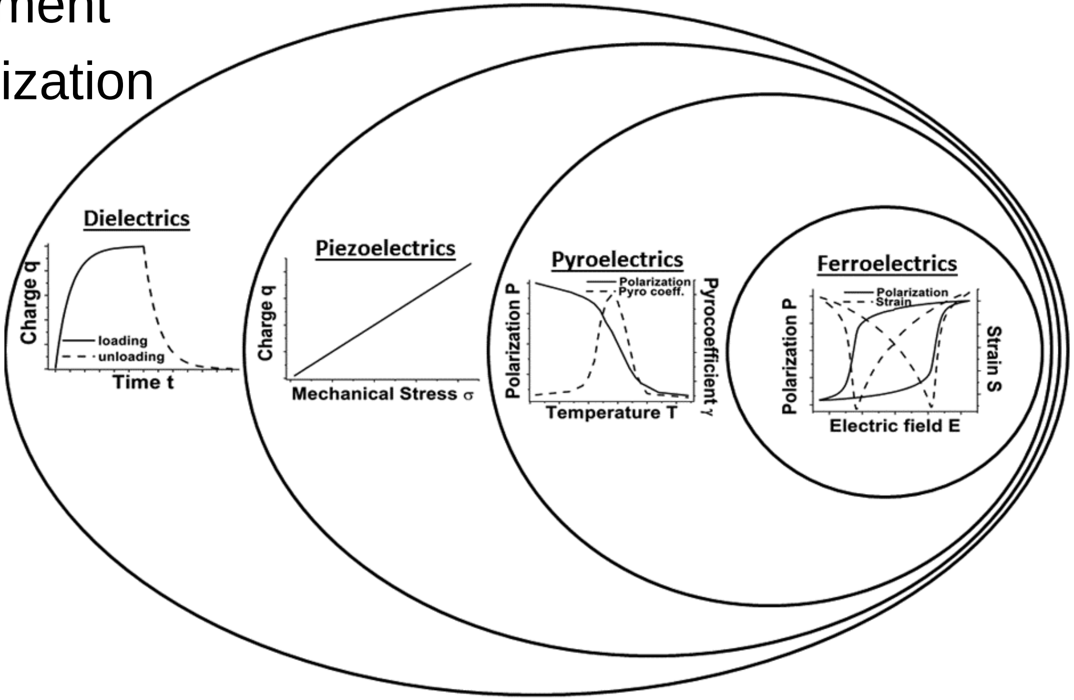
DFG

International Symposium on Electrical Fatigue in Functional Materials 15. – 18.09.2014,

Motivation

Ferroelectric ceramics combine the characteristics of dielectrics, piezoelectrics and pyroelectrics in additional to ferroelectric properties

- → High dielectric stability
- → Coupled strain and dipole moment
- → Temperature-dependent polarization
- → Switchable polarization

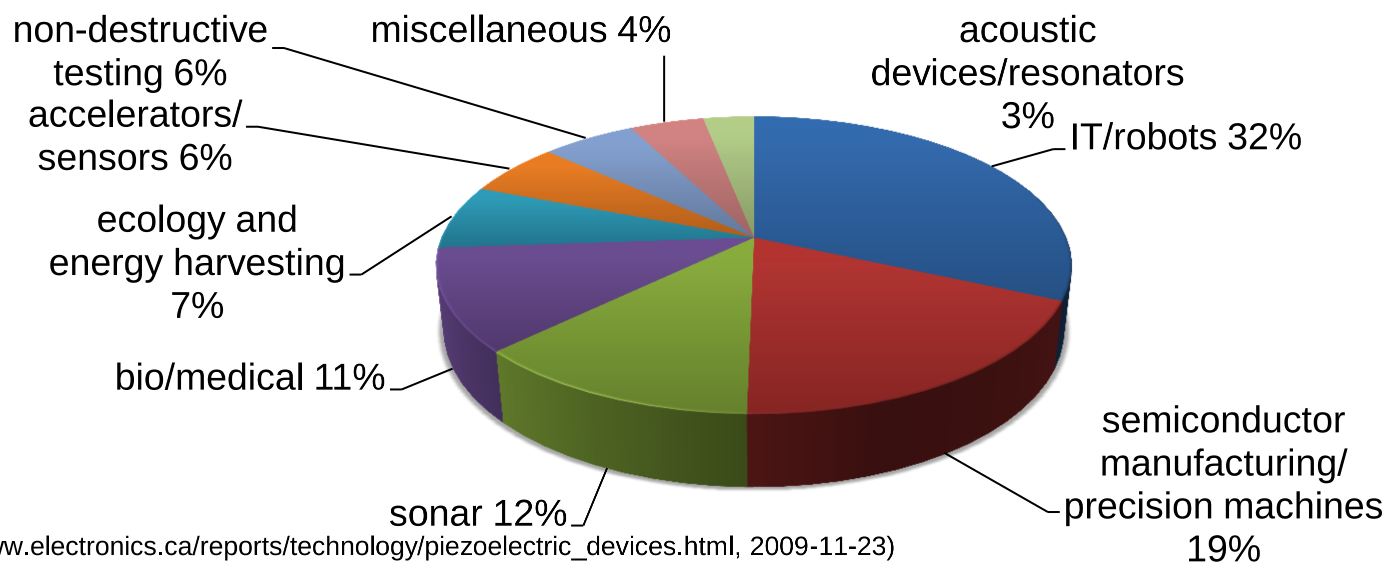


Motivation

Piezoceramic Applications

- High-tech applications: sonar systems, medical diagnostics, telescopes,…
- Every-day devices: mobile phones, cameras, microphones,…

Market share of piezoelectric materials in 2012: US$19.6 billion, piezoelectric actuators alone about US$6.5 billion in 2009



source: http://www.electronics.ca/reports/technology/piezoelectric_devices.html, 2009-11-23)

Acknowledgement: J Ackermann & J. Rödel

Motivation

- Many applications require cyclic input signal (electrical, mechanical, electromechanical)
- Long-term stability and reliability under cyclic loading is crucial
- Fatigue mechanisms have to be understood to be able to develop reliable components
- Research on <u>lead-free materials</u> focuses on improvement of strain and polarisation – not repeated use in applications

Gap in knowledge on fatigue of lead-free materials must be closed!

Fatigue characteristics

Electric fatigue of lead-based materials has been studied intensively

Electrical cycling can lead to:

- Degradation of dielectric and piezoelectric parameters
- Asymmetries in hysteresis loops
- Development of bias field

Bipolar cycling

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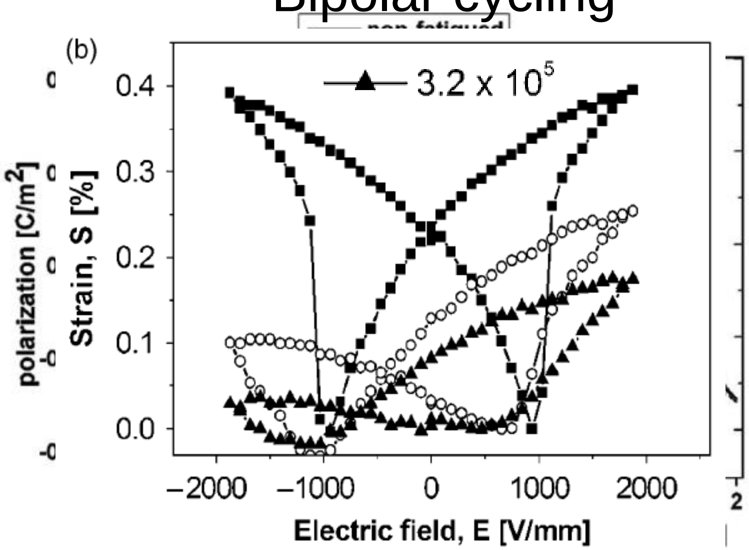
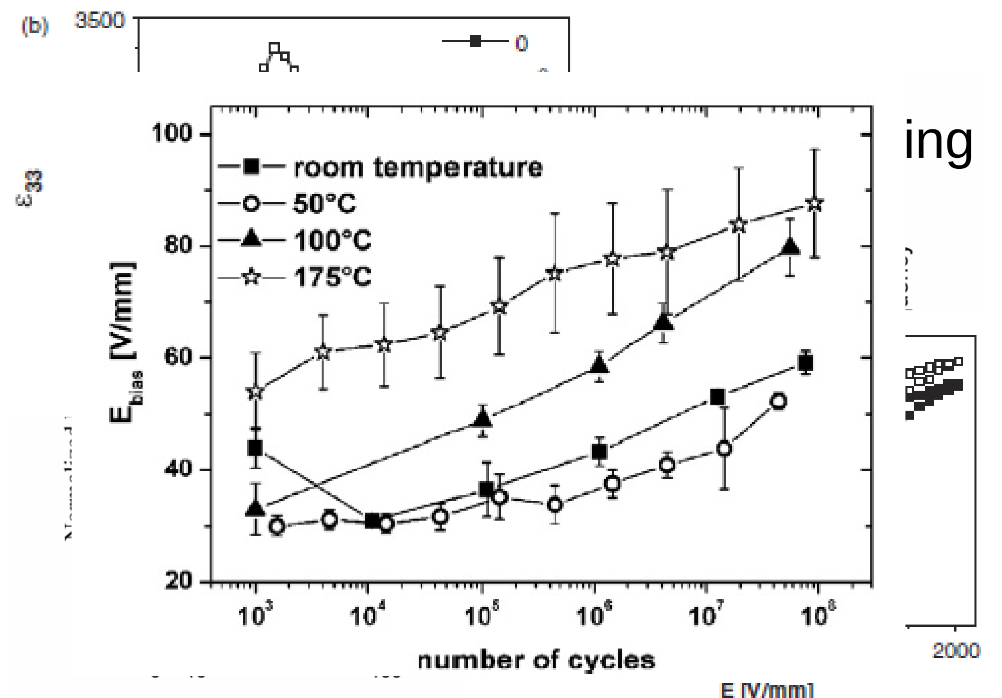




Glaum et al. *J. Appl. Phys.*, **2010**, 107, 104119

Balke et al., *J. Am. Ceram. Soc.*, **2007**, 90, 3869

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

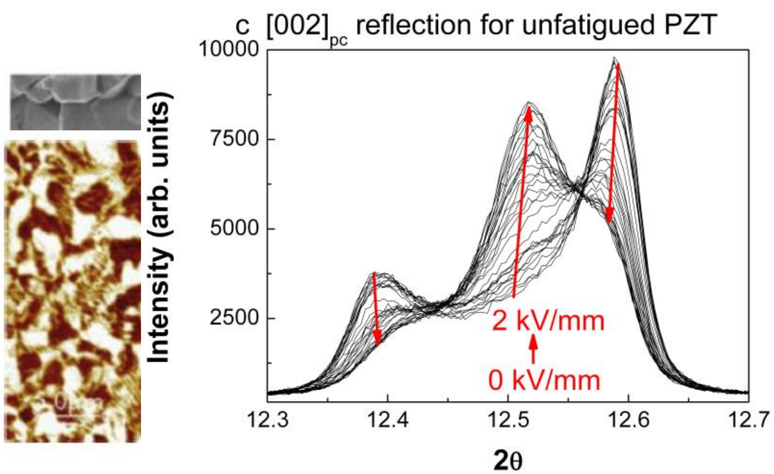
Balke et al., *J. Am. Ceram. Soc.*, **2007**, 90, 3869

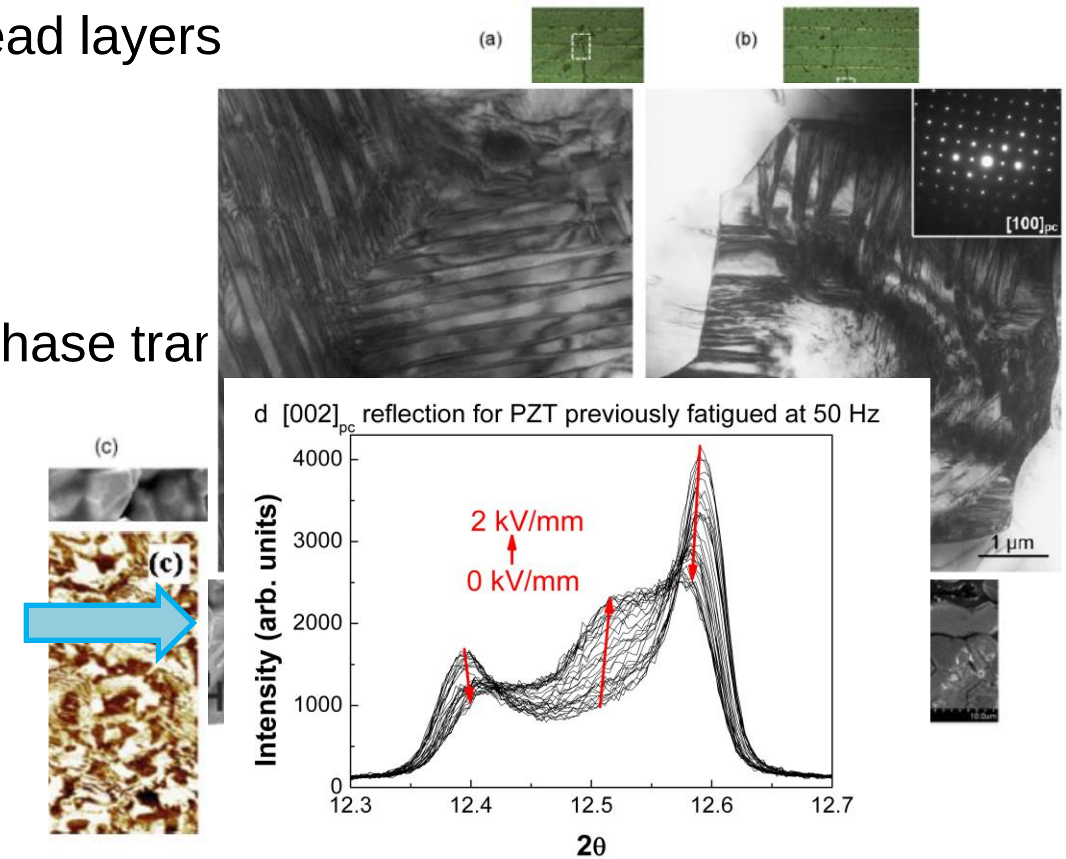
Rojprapai ..., *J. Eur. ...*, **2009**, ..., 1081

Fatigue characteristics

<u>Origins of electric fatigue</u>

- Development of cracks and dead layers
- Separation of the electrode
- Pinning of domain walls
- Miniaturization of domains
- Suppression of field induced phase trar





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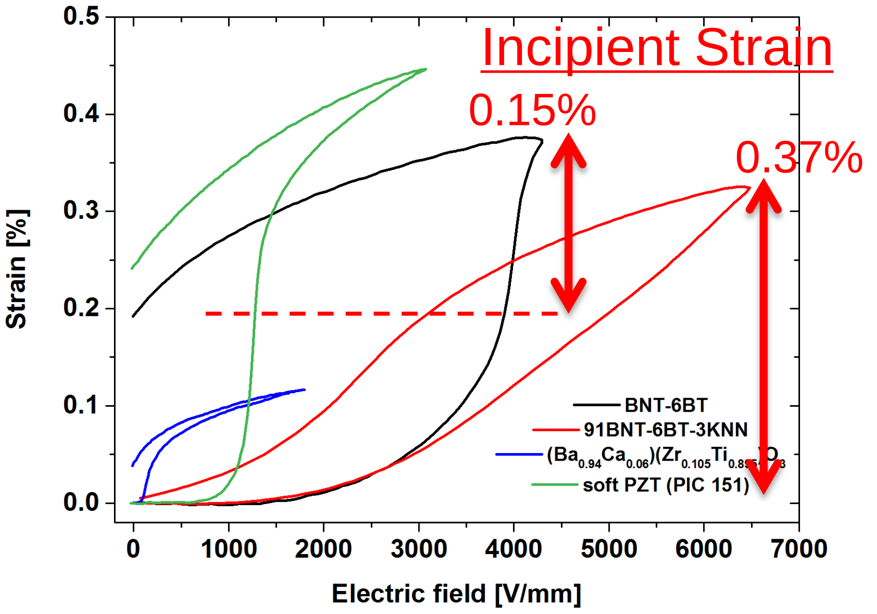
Lead-free ceramics

Research on lead-free replacements for PZT focussed on:

- $BaTiO_3$-based materials, e.g. $(Ba,Ca)(Zr,Ti)O_3$
- $(Bi,Na)TiO_3$-$BaTiO_3$
- $(K_{0.5}Na_{0.5})NbO_3$

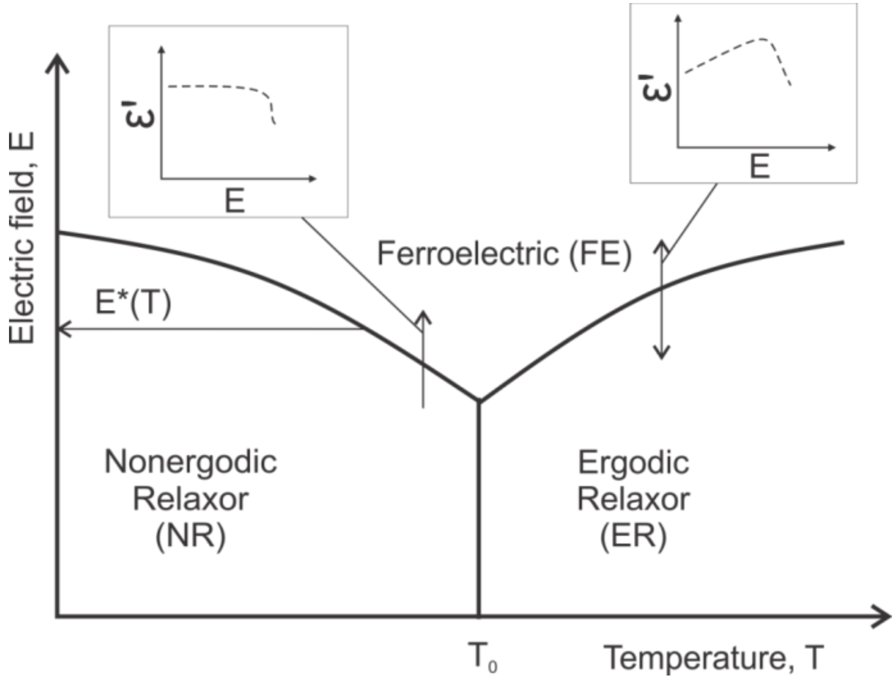
→ $(Bi,Na)TiO_3$-$BaTiO_3$-$(K,Na)NbO_3$

composition	d_{33} [pm/V]
Soft PZT	300-670
$BaTiO_3$	191
$(Bi,Na)TiO_3$-$6BaTiO_3$ (BNT-6BT)	122
93BNT- 6BT-1$(K,Na)NbO_3$	200
$Ba(Ti_{0.8}Zr_{0.2})O_3$-$(Ba_{0.7}Ca_{0.3})TiO_3$ (BCZT)	620
$(K_{0.5}Na_{0.5})NbO_3$ + Li, Ta, Sb (LF4)	300



Lead-free relaxor ceramics

Many promising lead-free compositions show relaxor-type behavior

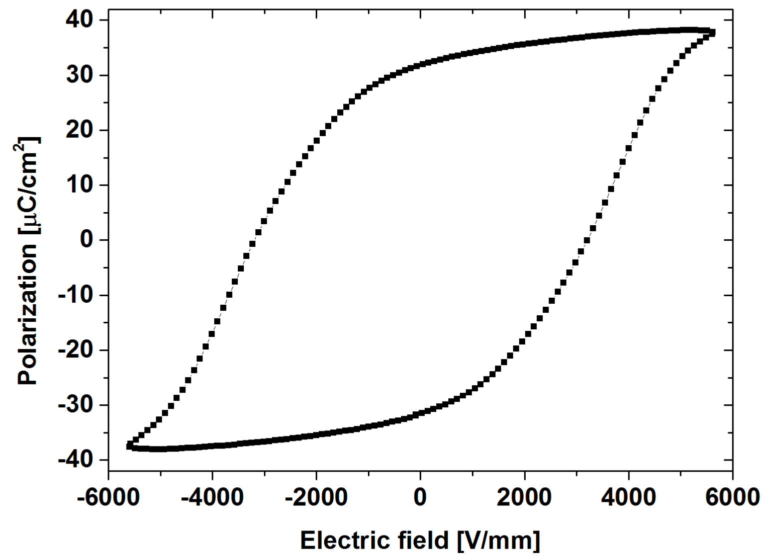


E-T behaviour plays important role in fatigue degradation

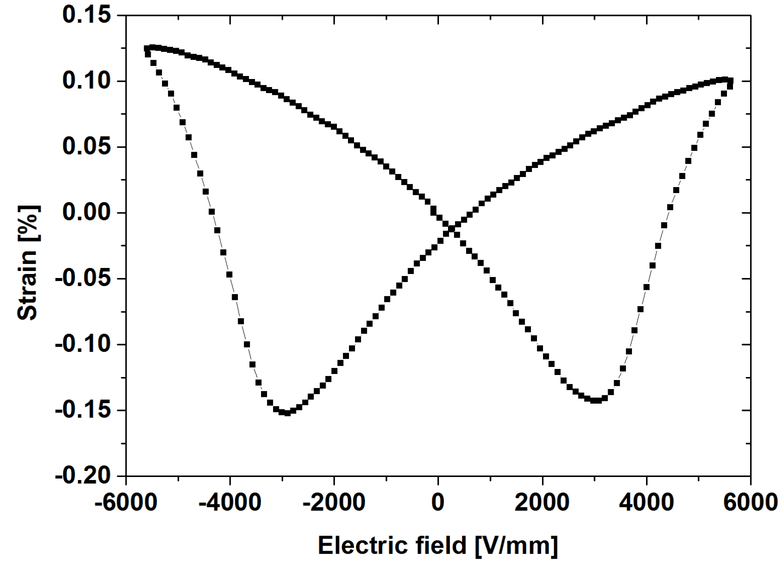
$(Bi,Na)TiO_3$-$BaTiO_3$

$(Bi,Na)TiO_3$-$BaTiO_3$-$(K,Na)NbO_3$

BNT-6BT
Macroscopic properties



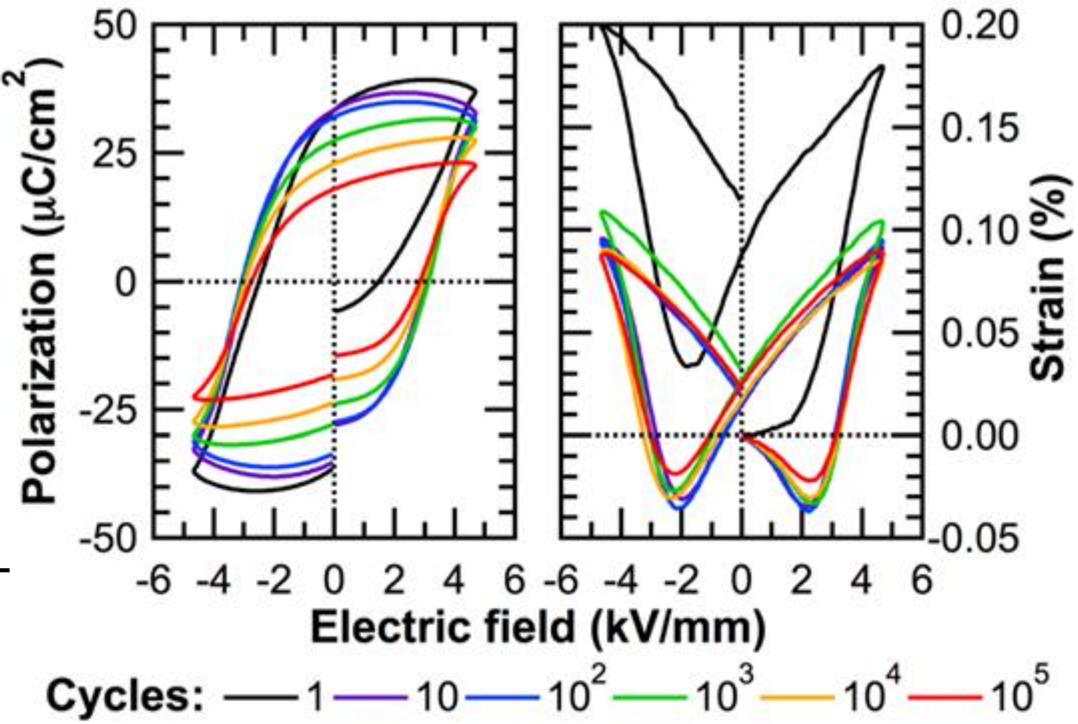
- Coercive field $E_c \sim 3$kV/mm
- Remanent polarization $P_r \sim 30\mu C/cm^2$
- Unipolar strain ~ 0.1% @ 5.5kV/mm



BNT-6BT
Bipolar fatigue

- Reduction of P_{max} and P_{rem}
- Reduction of negative strain

Significant fatigue of BNT-6BT



Simons et al., J. Appl. Phys. 112, 044101 (2012)

BNT-6BT
Bipolar fatigue

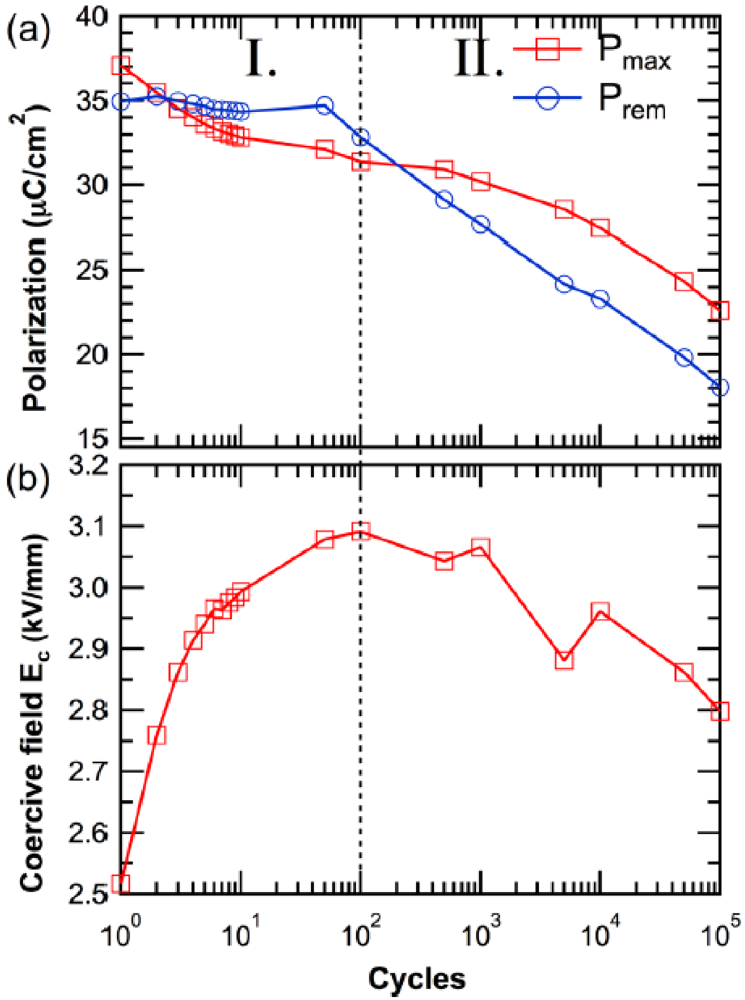
Two regions can be distinguished

Region I. (up to 100 cycles):

- Slight decrease of P_{max} and P_{rem}
- Increase of E_c

Region II. (more than 100 cycles):

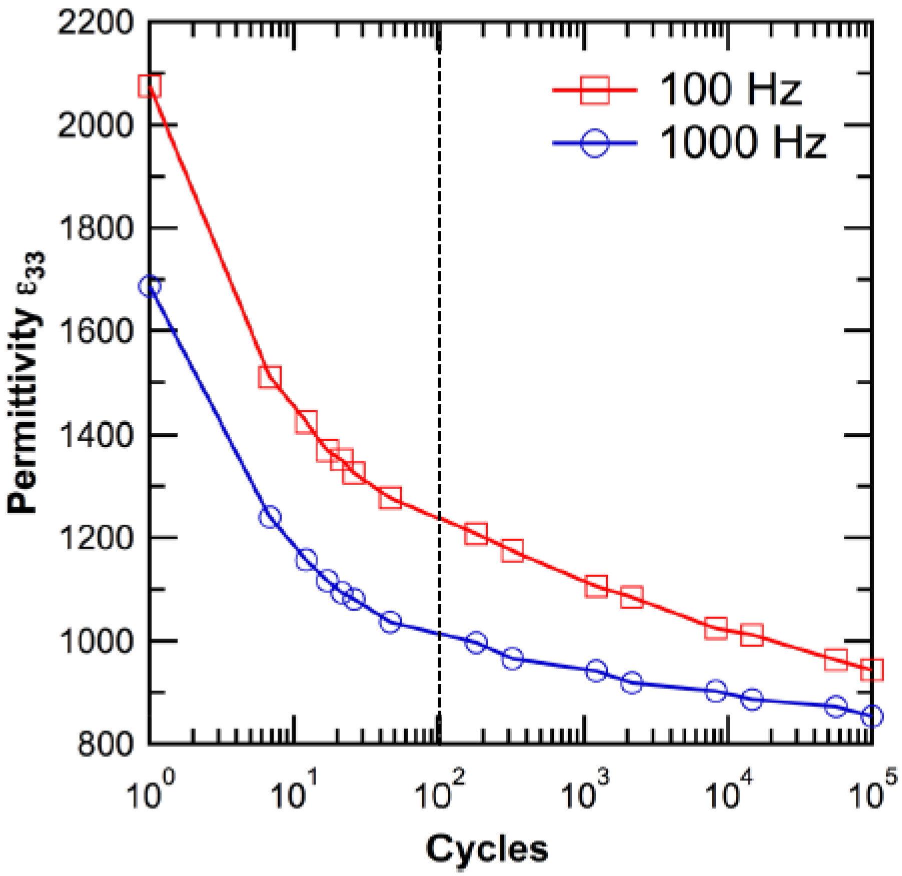
- Stronger decrease of P values
- Decrease of E_c



Simons et al., J. Appl. Phys. 112, 044101 (2012)

BNT-6BT
Bipolar faitgue

- Strong decrease up to 100 cycles
- Reduced rate of decrease above 100 cycles
- Frequency independent characteristic



Simons et al., J. Appl. Phys. 112, 044101 (2012)

BNT-6BT
Stuctural properties

Higher cycles:

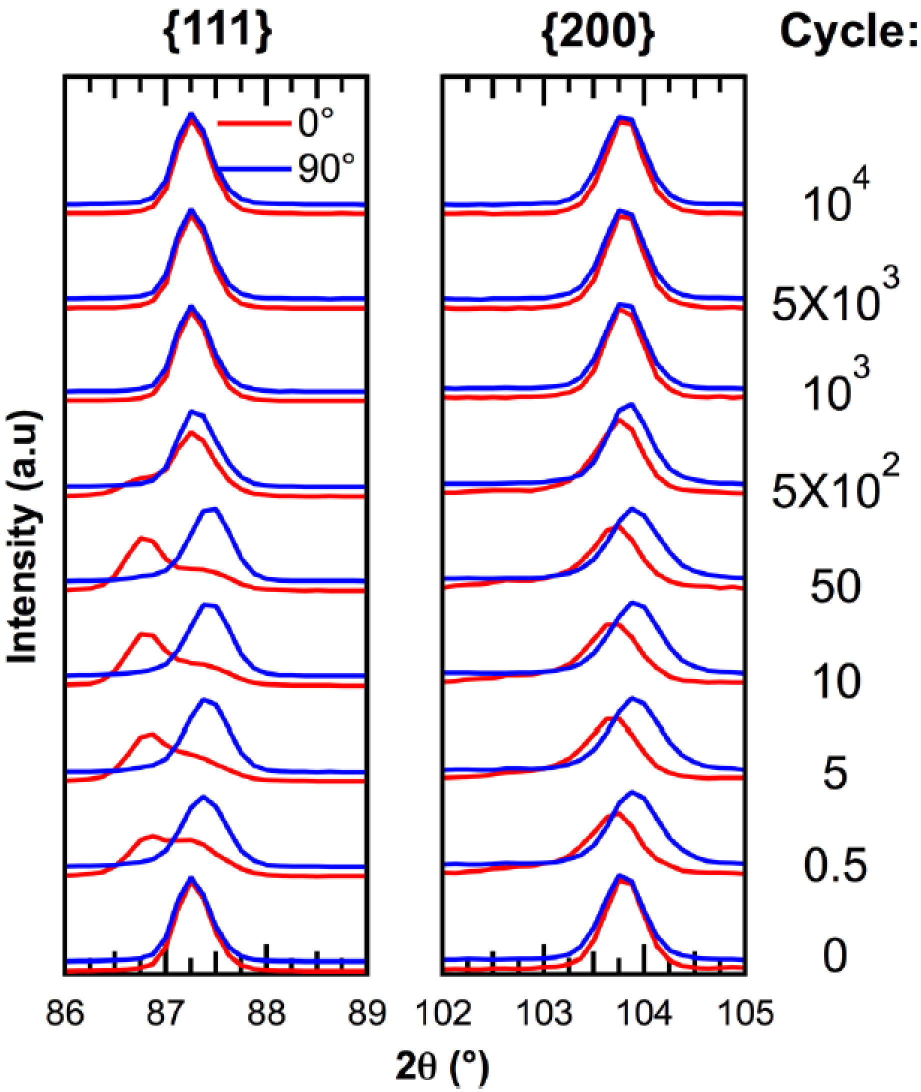
Long-range order destroyed, patterns appear pseudo-cubic again

Initial cycles:

Rhombohedral/tetragonal domain structures created

Unpoled state:

pseudo-cubic structure



Simons et al., J. Appl. Phys. 112, 044101 (2012)

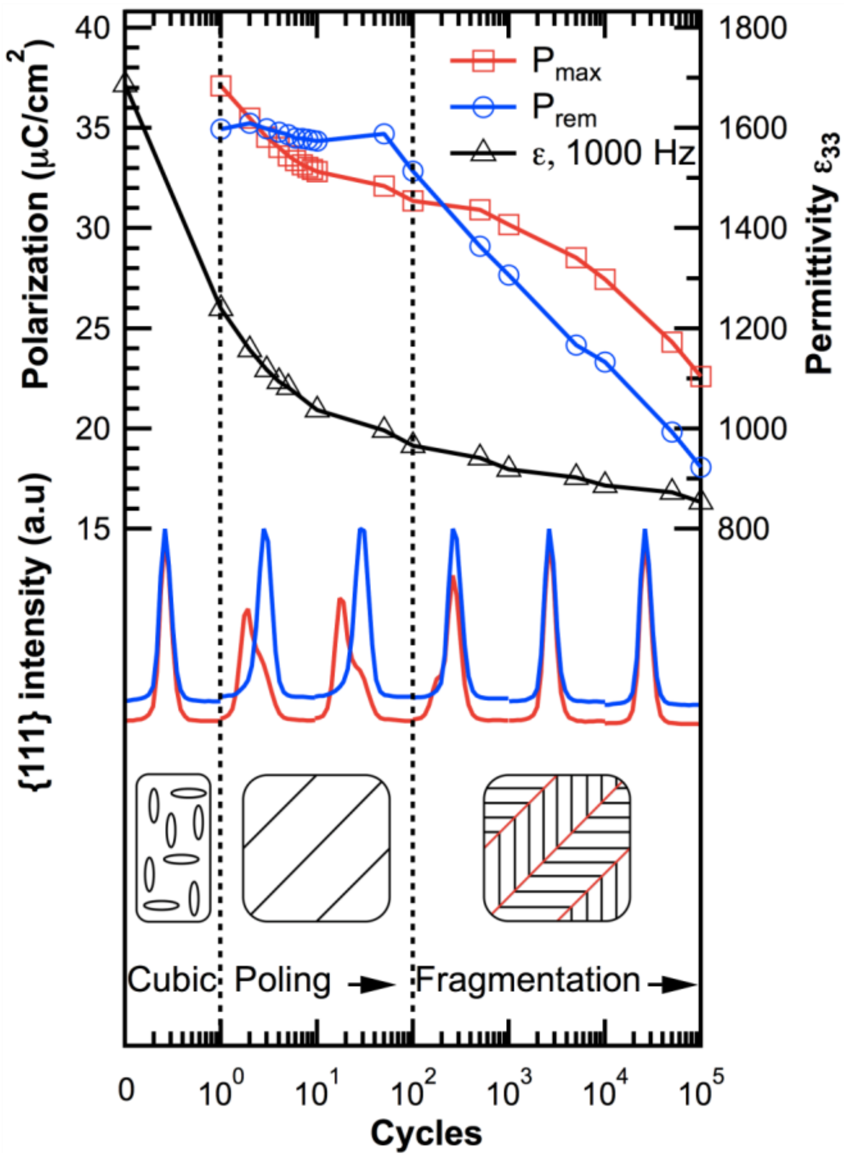
Fatigue mechanism

Fatigue process:

1. Defects migrate under bipolar electric fields
2. Domain walls pinned by defect agglomerates
3. New domain walls compensate internal fields

Fatigue effects:

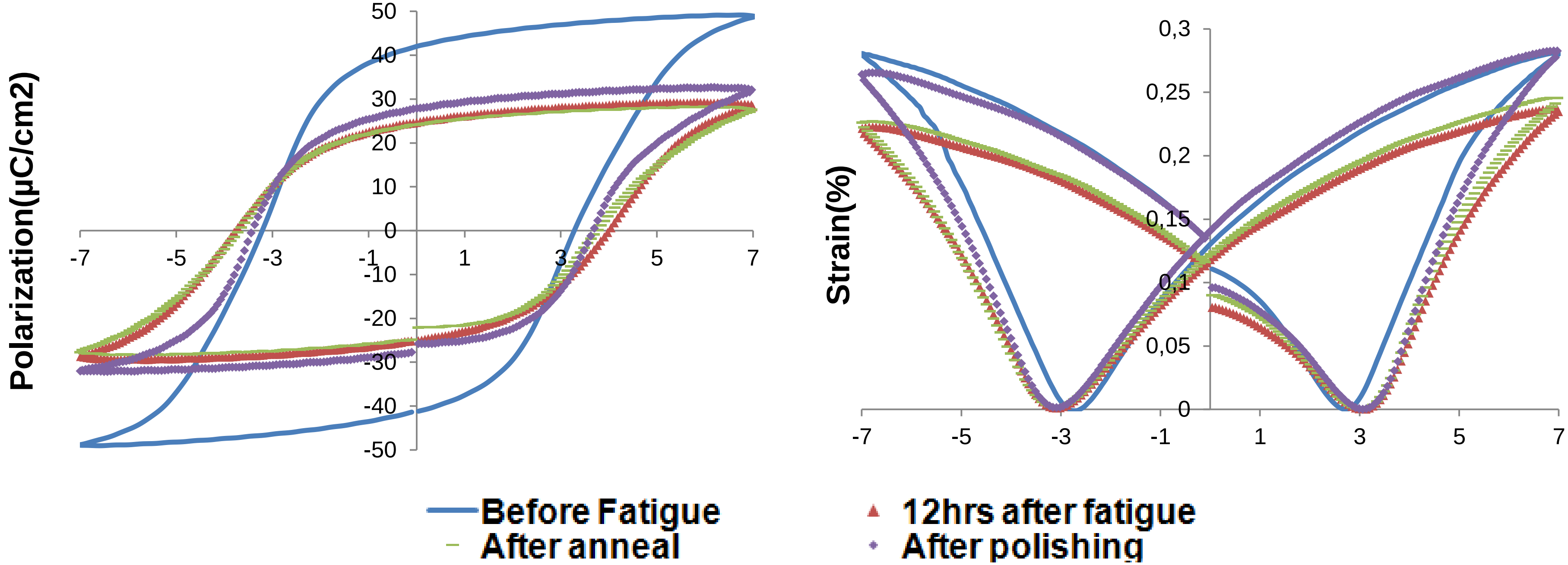
- Average domain size decreases
- Domain wall mobility decreases
- Polarization and strain decrease



Simons et al., J. Appl. Phys. 112, 044101 (2012)

Fatigue recovery: polishing effect

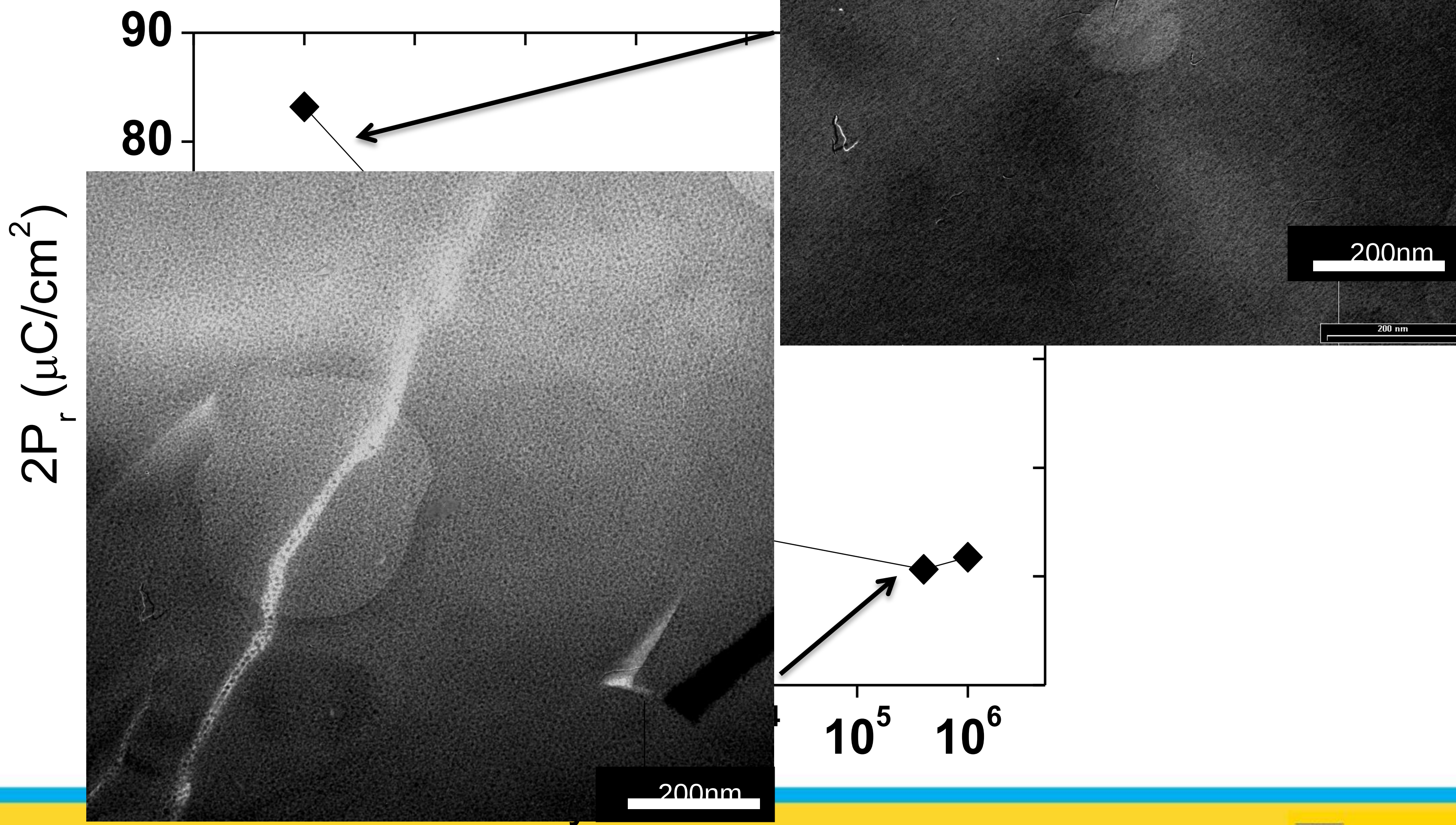
Bipolar cycling for 10^6 cycles
Then removal of ~150μm material near electrodes



Z. Luo at el, J. *Am. Ceramic Soc.*, 95**,** (2012), 2593

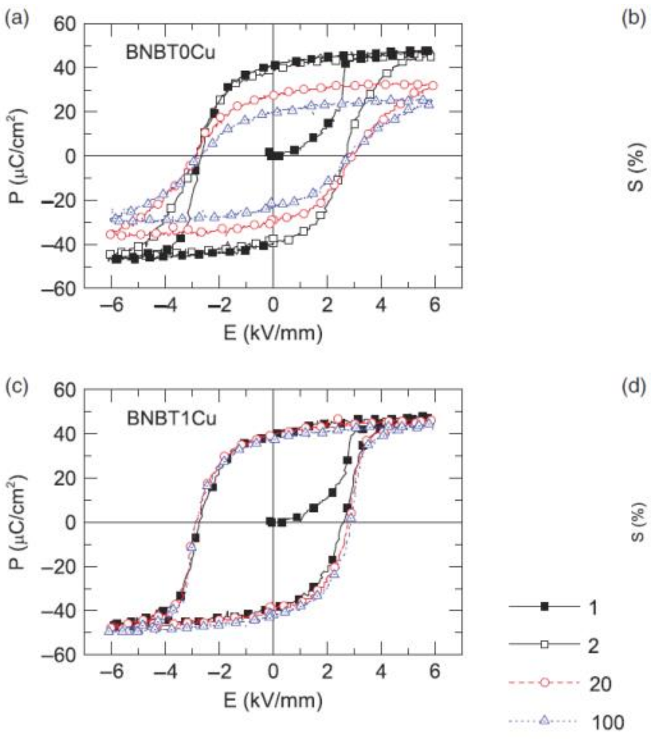
Changes in microstructure

Near-electrode regions



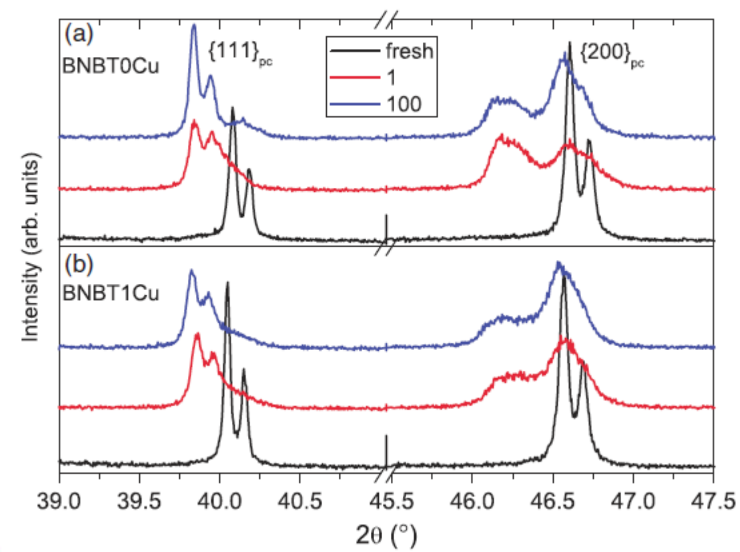
BNT-6BT + Cu

Improvement of cyclic stability by addition of 1 mol% Cu



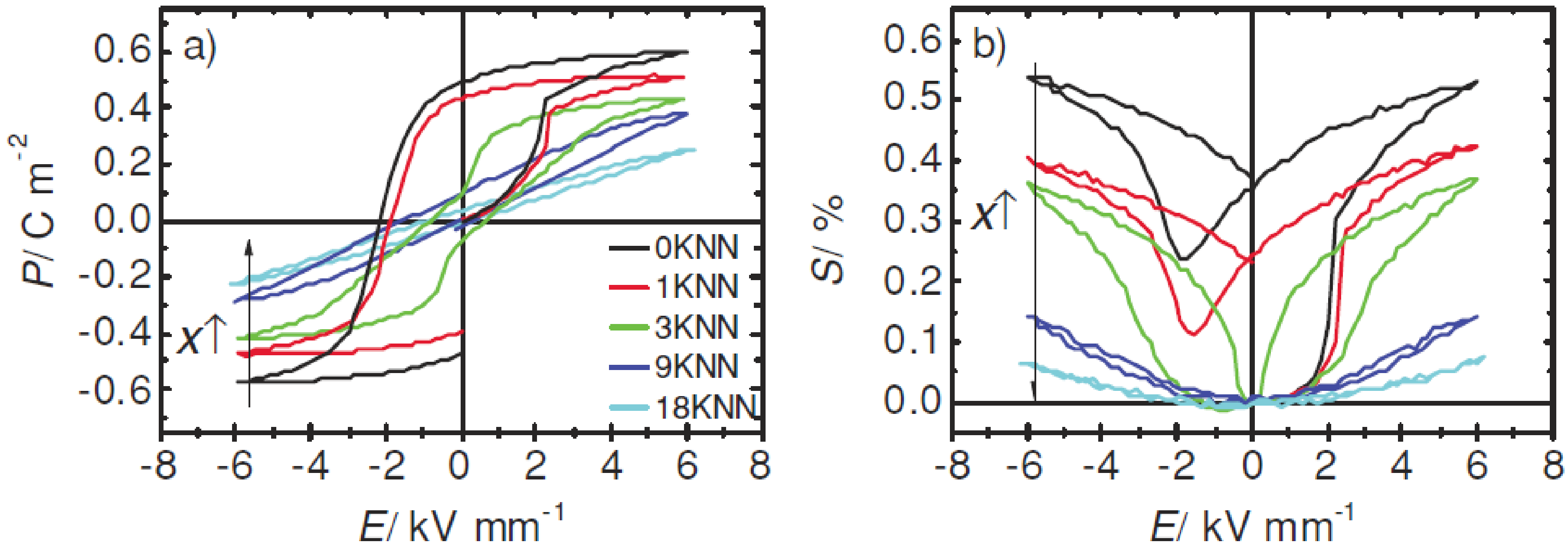
Cu-doped samples show:

- no crack development
- no continuous phase transition during cycling



Ehmke et al., *J. Am. Ceram. Soc.*, **2011**, *94*, 2473-2478

BNT-BT-KNN
Macroscopic properties



Addition of KNN to BNT-6BT leads to

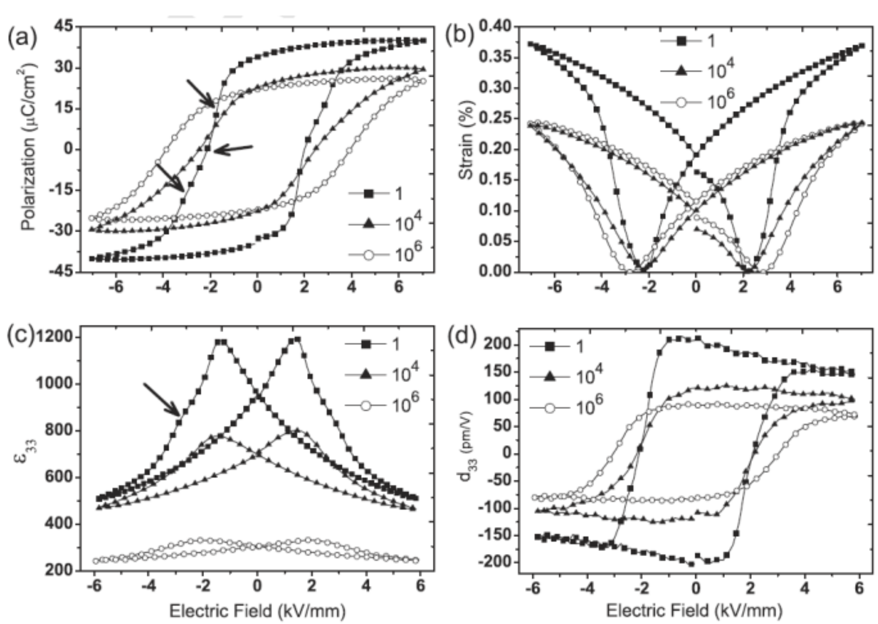
- pinching of the polarization loops
- development of “sprout” shape strain hysteresis

Dittmer et al., *Adv. Func. Mater.*, **2012**, *22*, 4208-4215

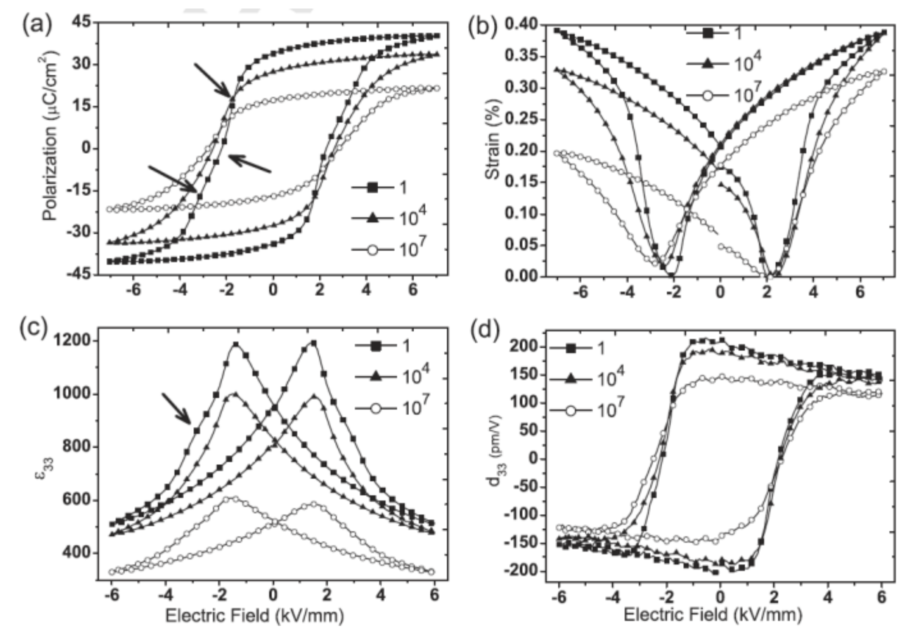
BNT-BT-KNN
Fatigue characteristics

93BNT-6BT-**1**KNN

- Similar bipolar and unipolar fatigue characteristics to BNT-6BT
- Unfatigued hysteresis loops show slight anomalies
- Fits model of charge carrier accumulation and domain wall pinning



Bipolar cycling



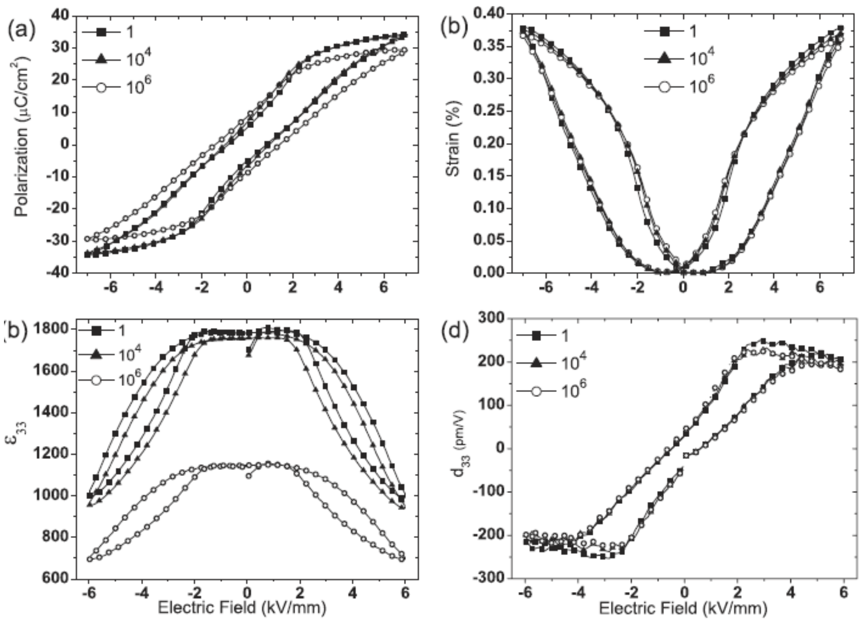
Unipolar cycling

Z. Luo et al, *J. Am. Ceramic Soc.*, 94**,** (2011), 3927

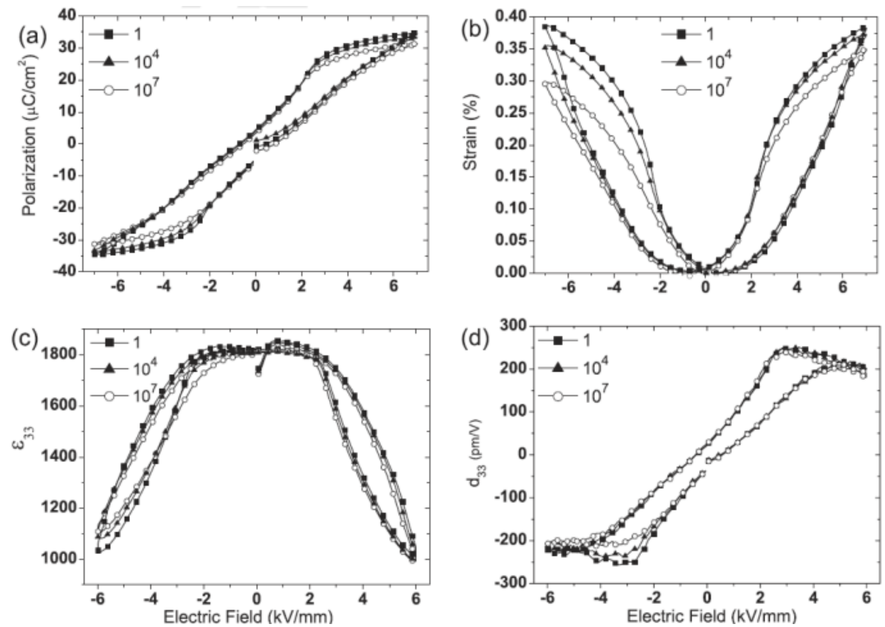
BNT-BT-KNN Fatigue characteristics

91BNT-6BT-**6**KNN

- Unfatigued loops are strongly pinched
- Only slight changes due to unipolar and bipolar cycling



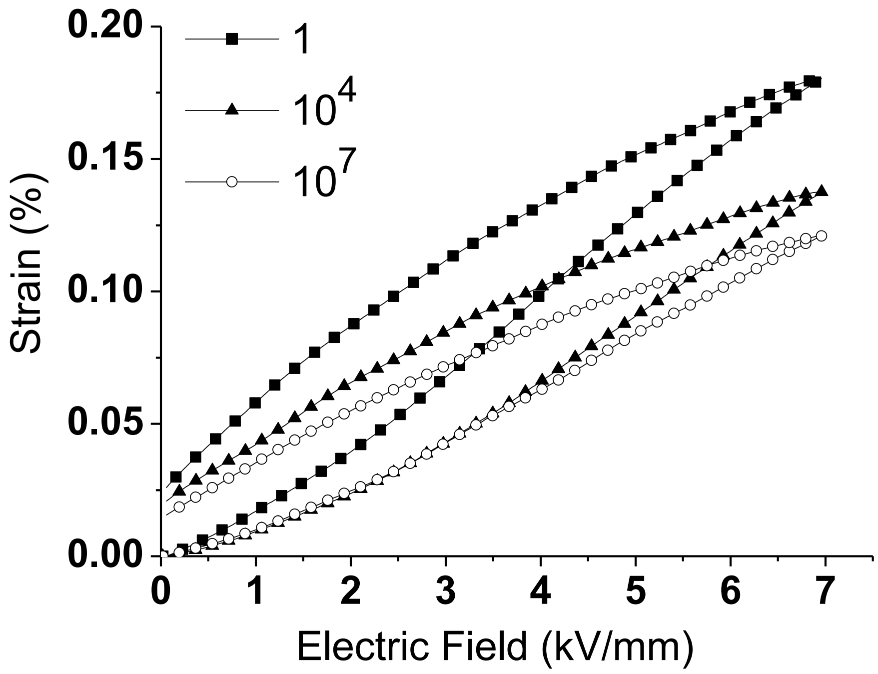
Bipolar cycling



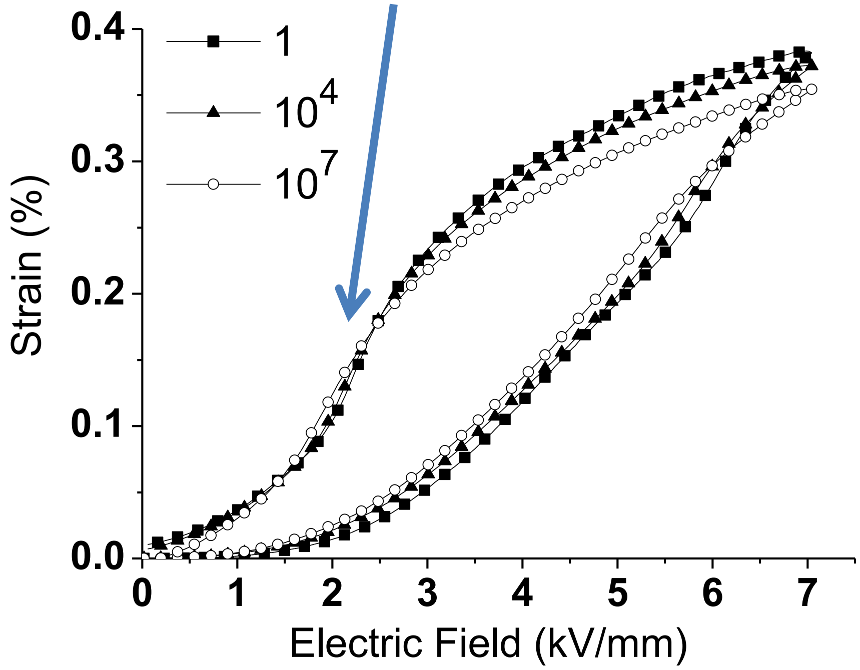
Unipolar cycling

Origins of fatigue

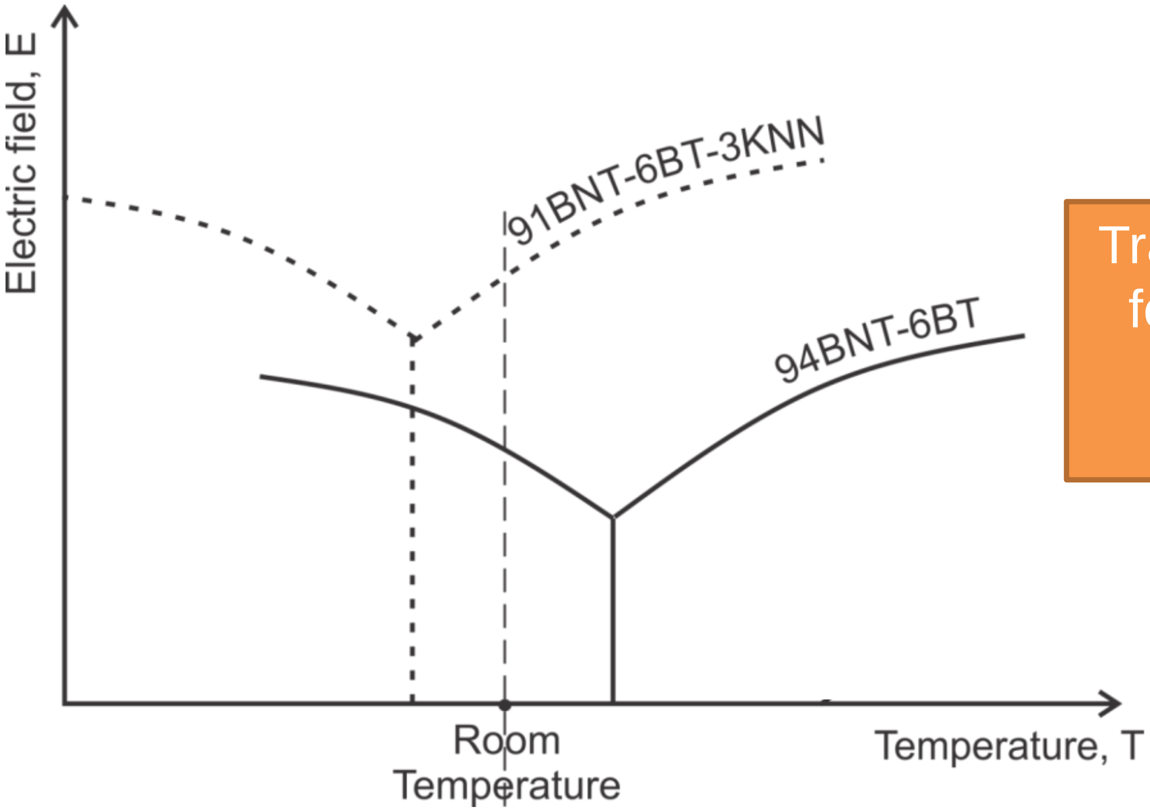
94BNT-6BT



91BNT-6BT-3KNN



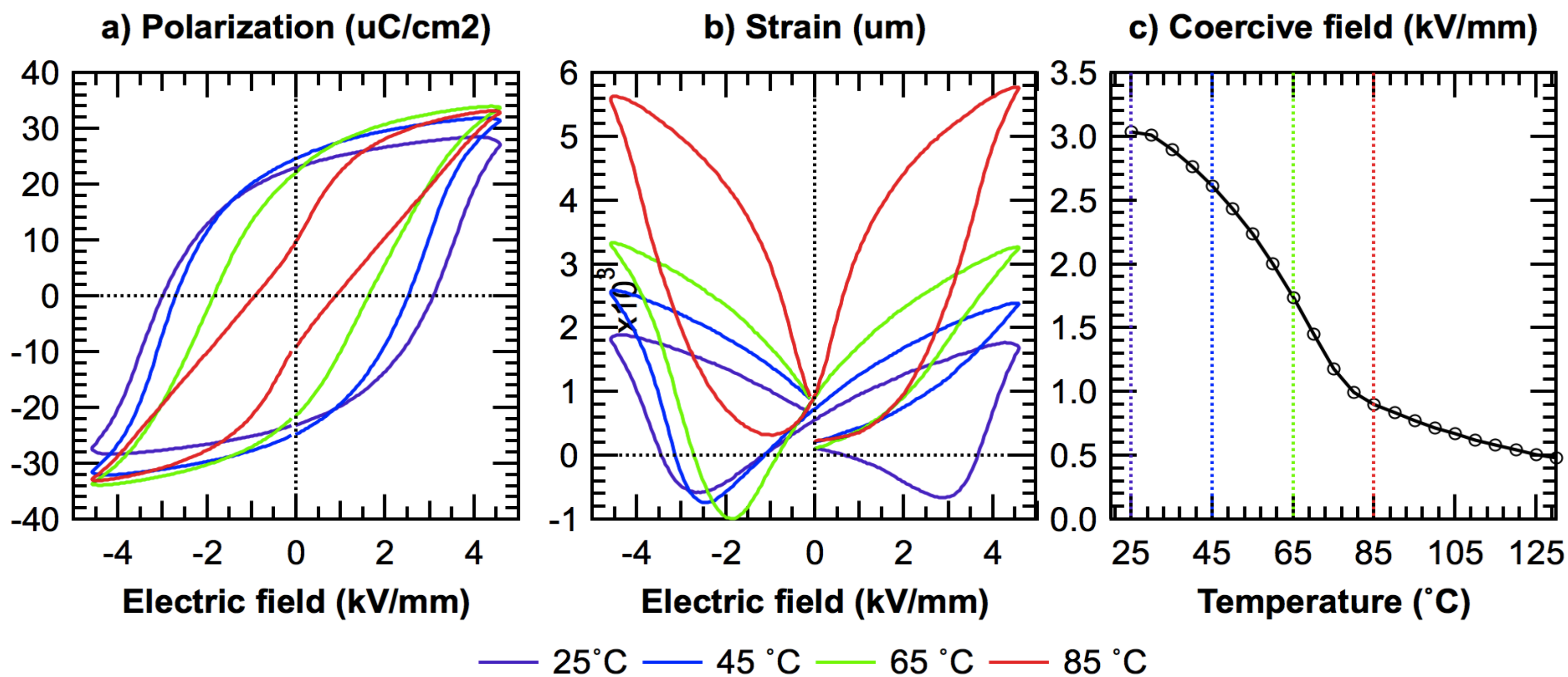
BNT-BT based materials: Fatigue Mechanism



Transition temperature between ferroelectric and relaxor state determines susceptibility to cyclic fatigue

BNT-6BT should be fatigue-free at higher temperatures

BNT-6BT
Temperature-dependent properties



Transition from non-Ergodic → Ergodic relaxor @ T_0=83°C

- Electric field induced transformation becomes reversible
- i.e. destabilization of the ferroelectric phase when electric field removed

Experimental

Bipolar fatigue: f = 10 Hz, $E_{max} = 1.5\ E_c$

Temperatures: 25°C, 45°C, 65°C, 85°C

Electrical

Polarization/Strain: f = 10 Hz, $E_{max} = 1.5\ E_c$

Permittivity ε_{33} *:* f =$10^3/10^4$ kHz, E_{AC}=10 V/mm

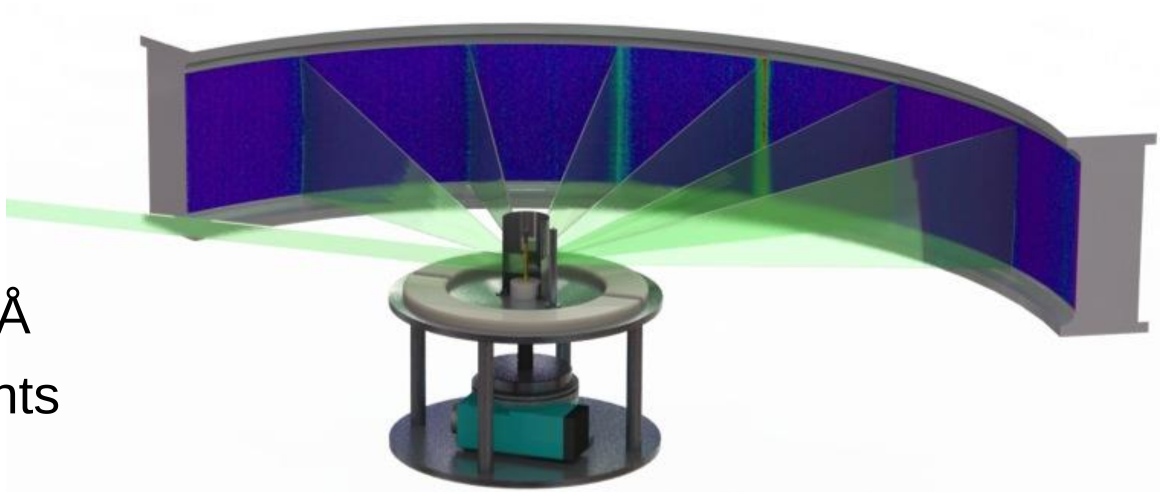
STRUCTURAL

Wombat (ANSTO, Australia)

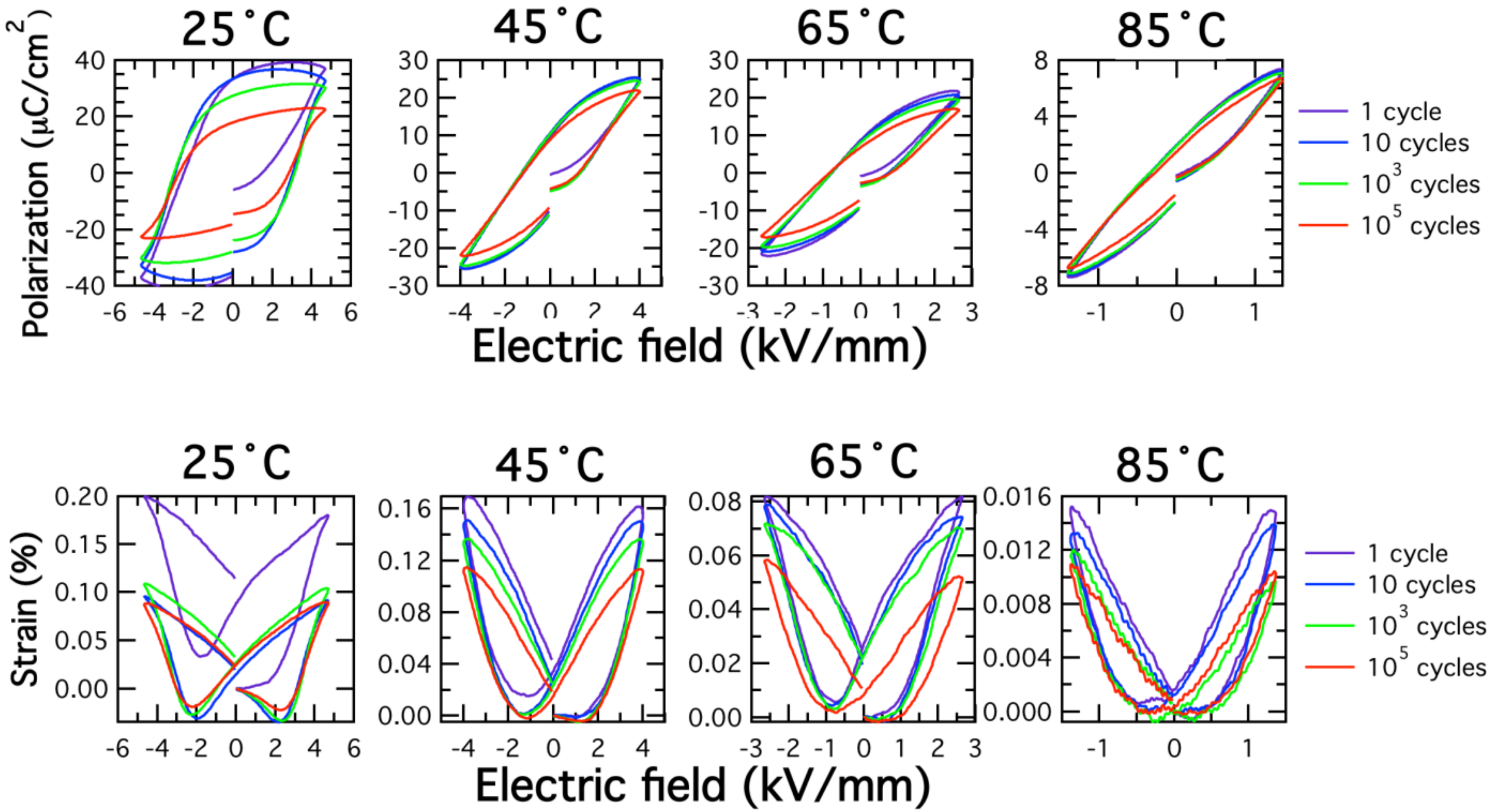
Neutron diffraction:

Constant wavelength: λ=2.95Å

Texture: 180° @ 10° increments



BNT-6BT
Temperature-dependent fatigue

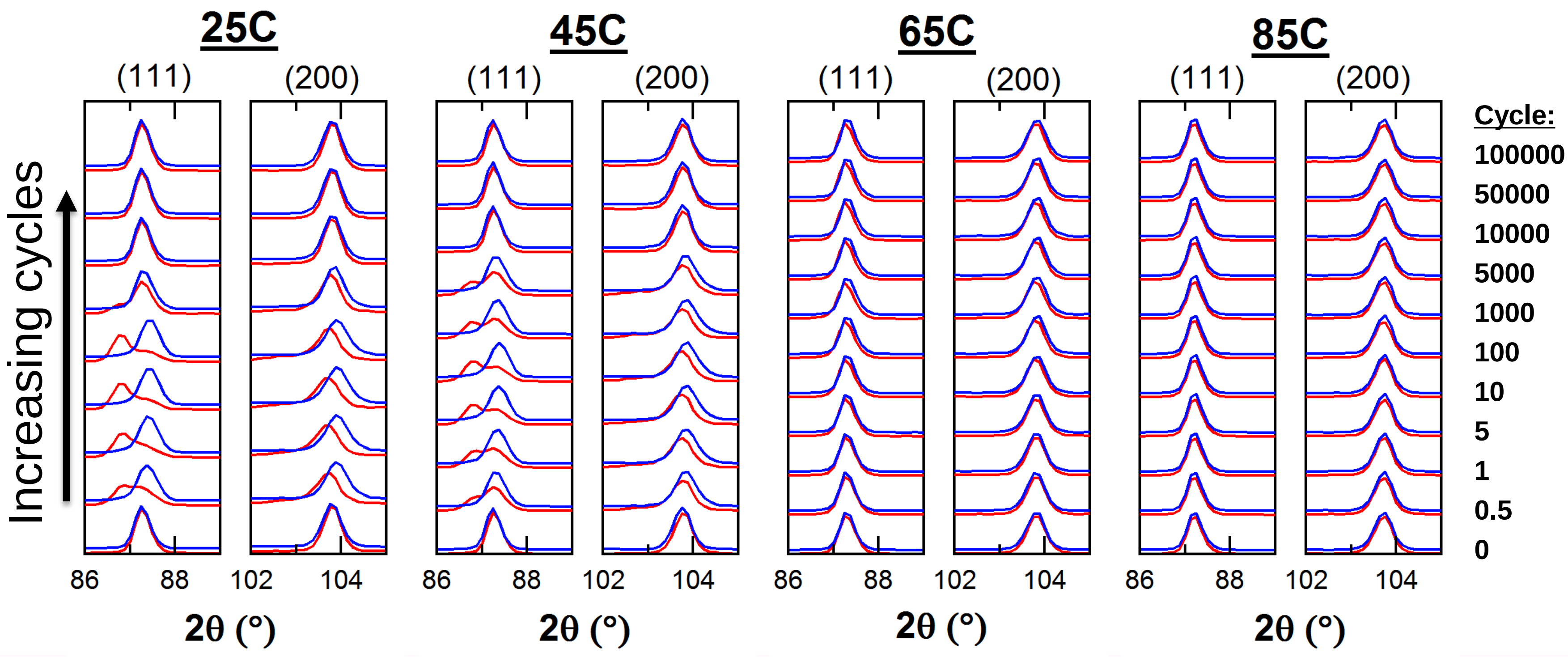


Structure measurements

Initial cycles: Rhombohedral/tetragonal domain structures created

Higher cycles: Domains fragment, long-range order destroyed

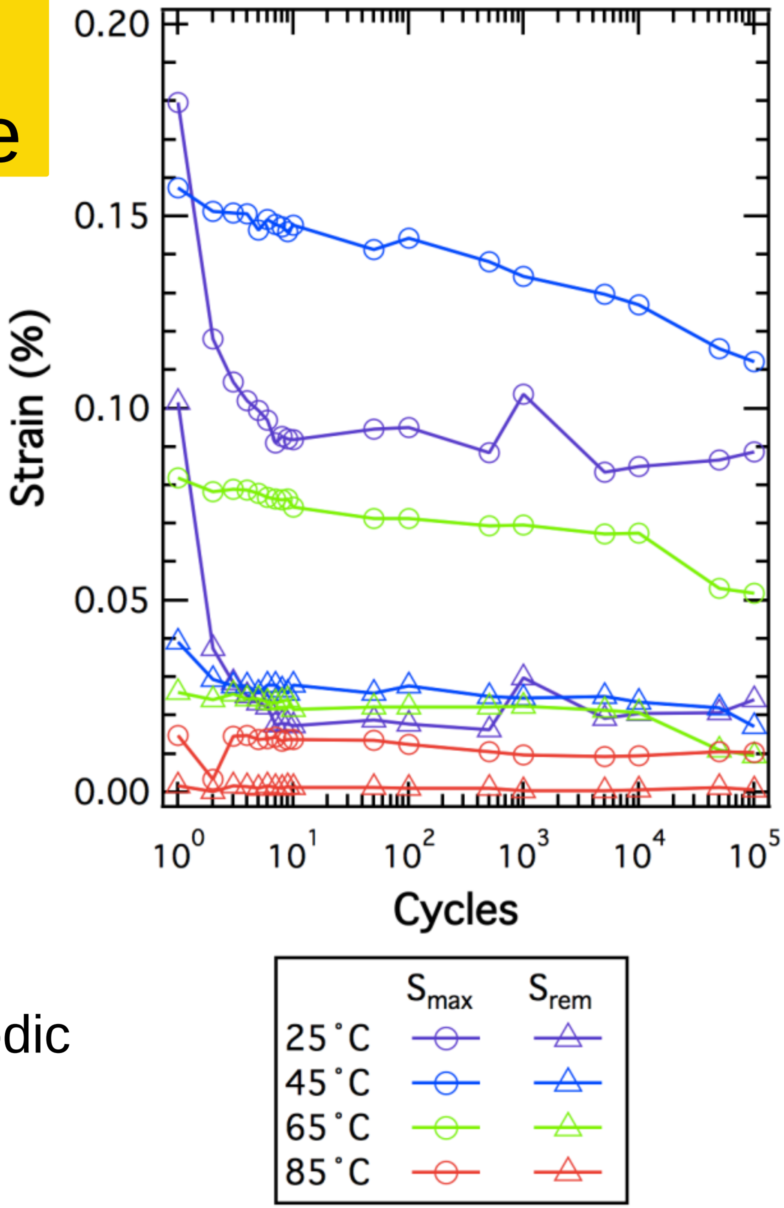
Increasing temperature: Poling more difficult, but persists longer



BNT-6BT
Temperature-dependent fatigue

<u>25°C (Ferroelectric/Non-Ergodic):</u>

- Initial strain decrease due to ferroelectric →relaxor transition



<u>45-85°C (Non-Ergodic→Ergodic)</u>

- Fatigue at 45 & 65°C
- Rate of fatigue decreases as temperature increases
- <u>I.e.</u> rate of fatigue decreases as Non-Ergodic → Ergodic transition approached

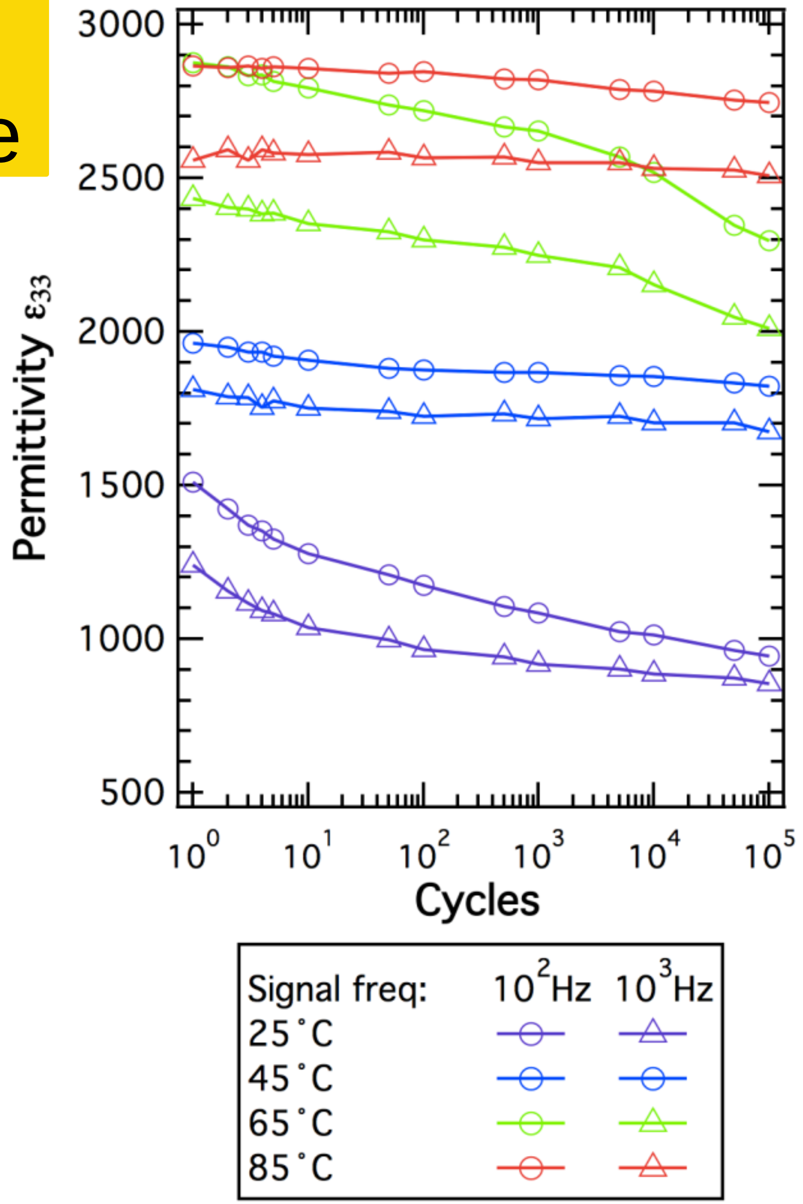
BNT-6BT
Temperature-dependent fatigue

<u>25°C (Ferroelectric/Non-Ergodic):</u>

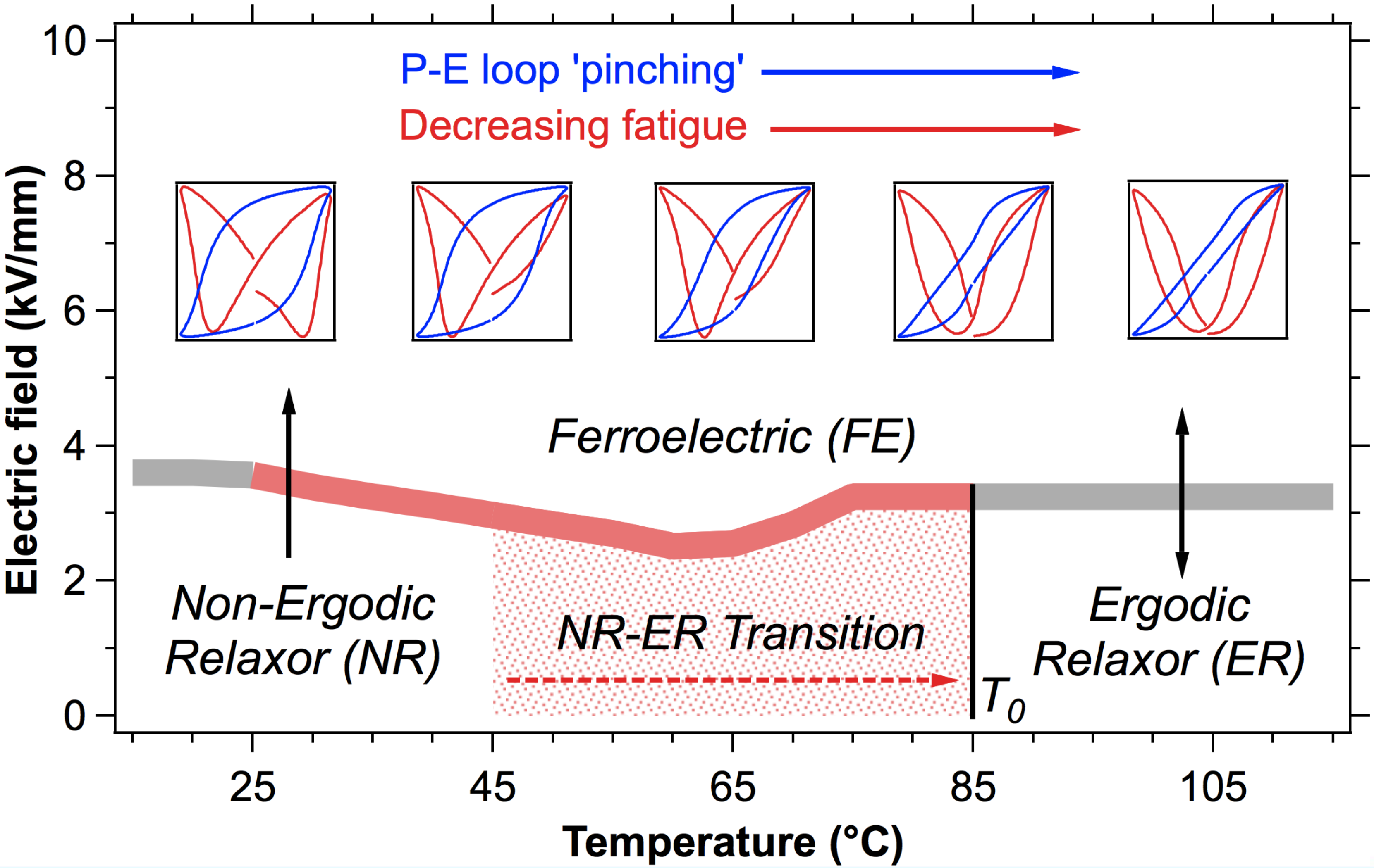
- ε_{33} decrease in initial cycles due to relaxor→ferroelectric transition
- Steady-state ε_{33} fatigue after 10^2 cycles

<u>45-85°C (Non-Ergodic→Ergodic)</u>

- Permittivity increases with temperature
- Transition from ferroelectric→relaxor
- Initial ε_{33} drop lessens with temperature: i.e. less material transforming to ferroelectric state near transition



Non-Ergodic→Ergodic transition



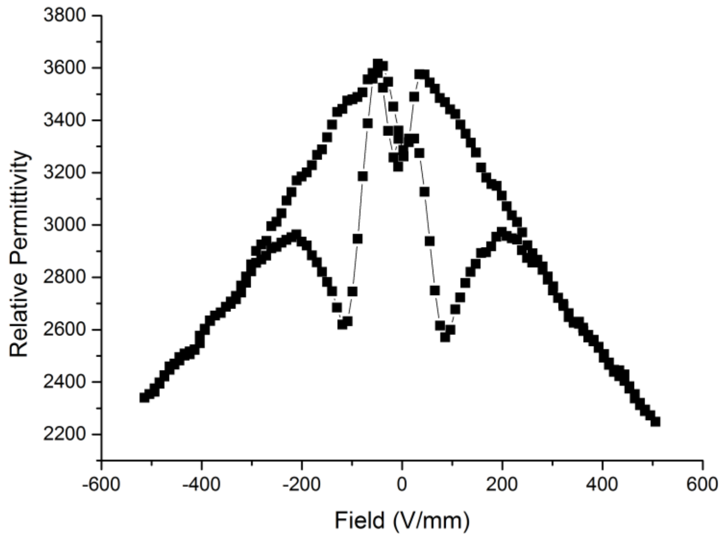
Ferroelectric lead-free ceramic $(Ba,Ca)(Zr,Ti)O_3$

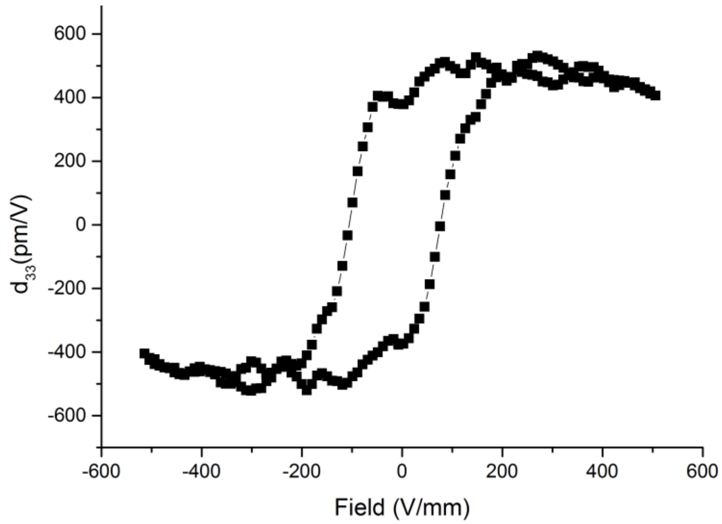
- Ferroelectric for Zr content < 20%
- Shows relaxor features for higher Zr content

- Low coercive field
- Remanent Strain ~ 12μC/cm^2
- Maximum Strain < 0.1%

Permittivity ε_r and piezoelectric coefficient d_{33} comparable to soft PZT

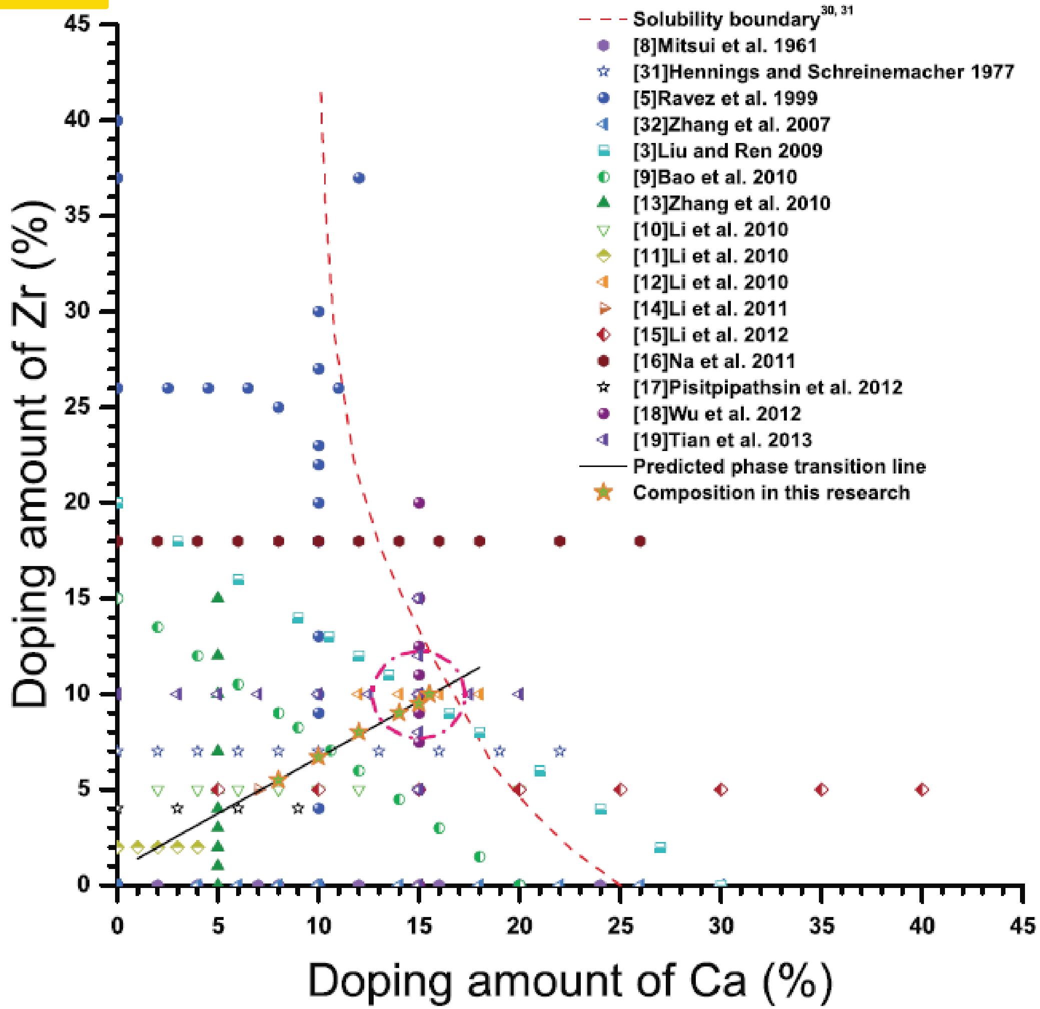
$BC_{15}Z_{10}T$





BCZT
d_{33} vs. composition

Compositions along tie line show highest piezoelectric coefficient d_{33}

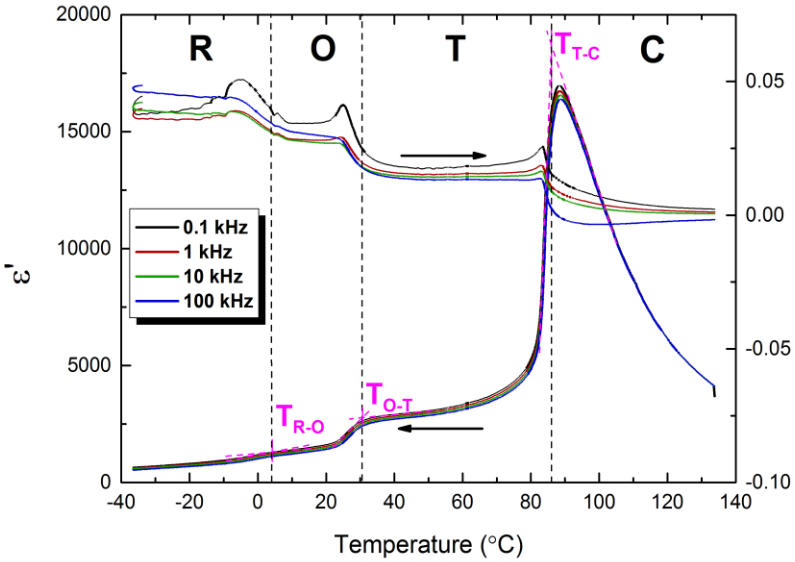


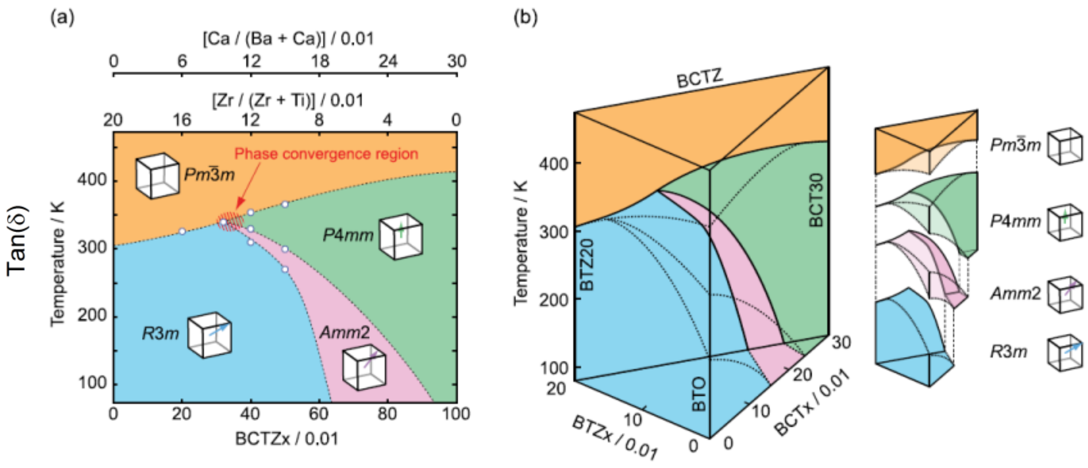
Y. Zhang et al., *J. Amer. Ceram. Soc.*, **2014**, *97*, 2885

BCZT
Phase transitions

All investigated compositions show rhomb.→ orth.→tetr. transitions around room temperature

$BC_{15}Z_{9.5}T$

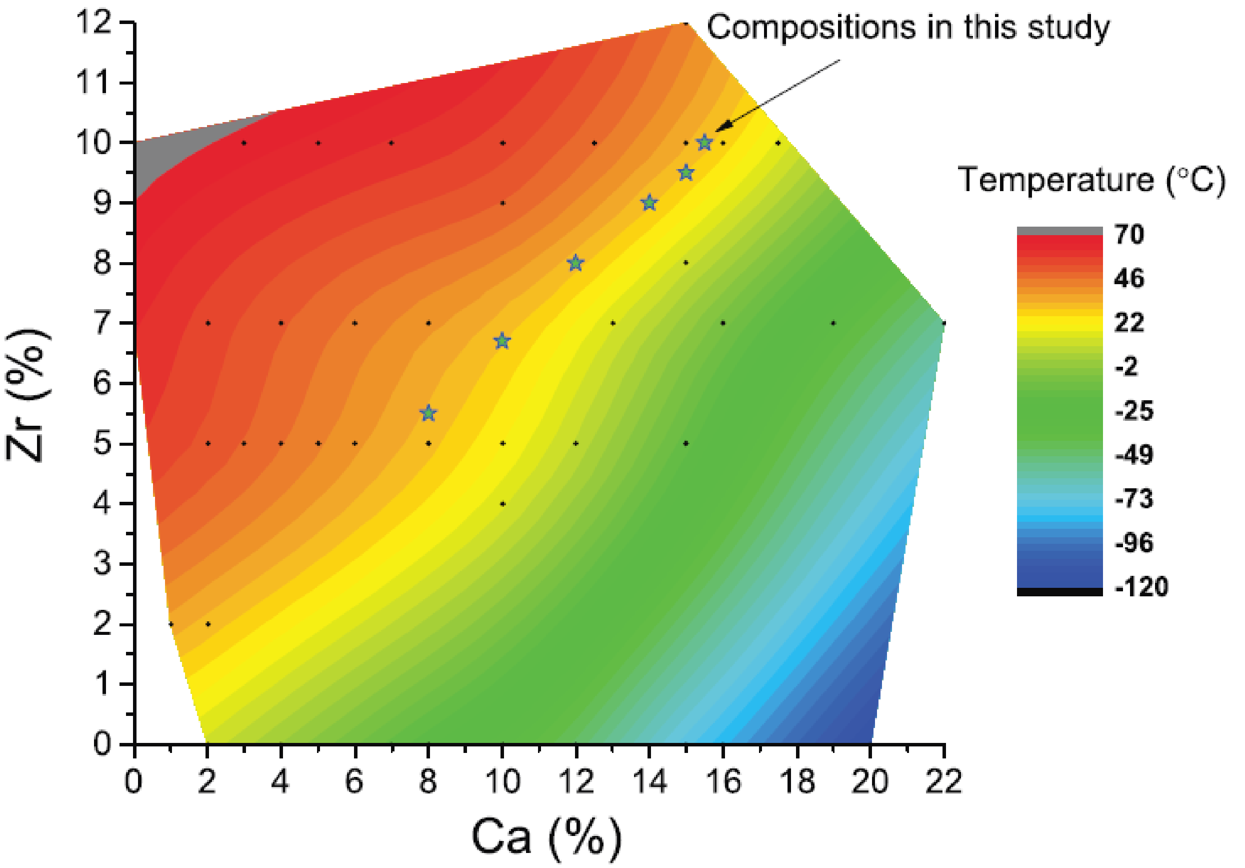




Zhang et al., *J. Amer. Ceram. Soc.*, **2014**, *97*, 2885   Keeble, *Appl. Phys. Lett.*, **2013**, *102*, 092903

BCZT
Phase transitions

Orthorhombic-tetragonal phase transition temperature

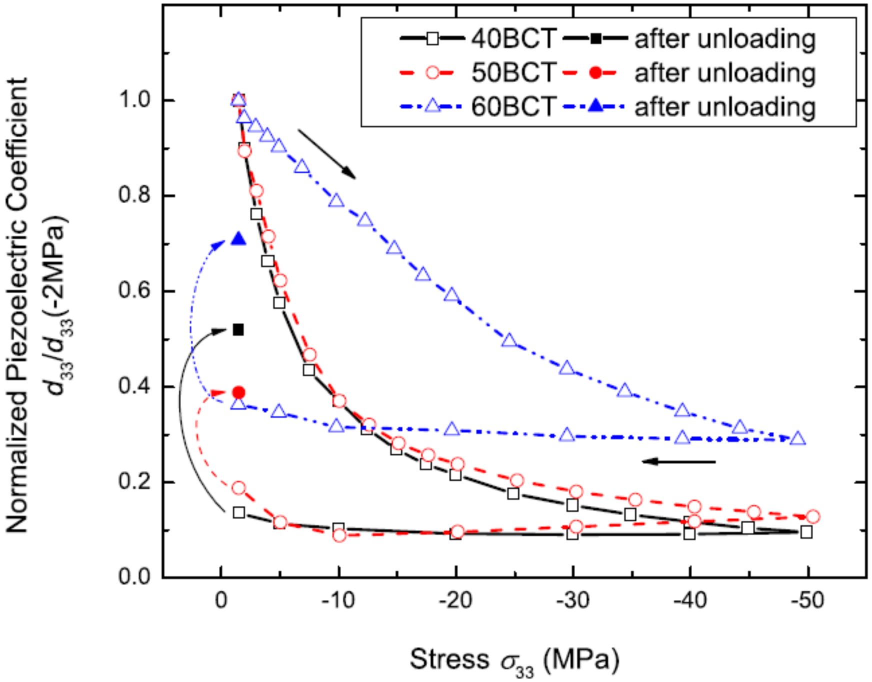


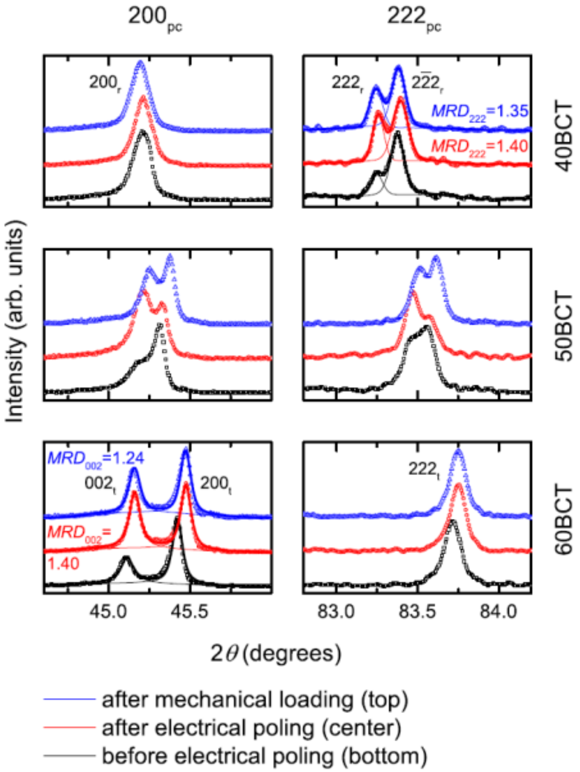
Zhang et al., *J. Amer. Ceram. Soc.*, **2014**, *97*, 2885

BCZT
Mechanical pressure

Piezoelectric performance is susceptible to mechanical loading

- rhombohedral and MPB compositions more than tetragonal ones
- reduction in d_{33} determined by ferroelastic switching and reduction of domain wall density

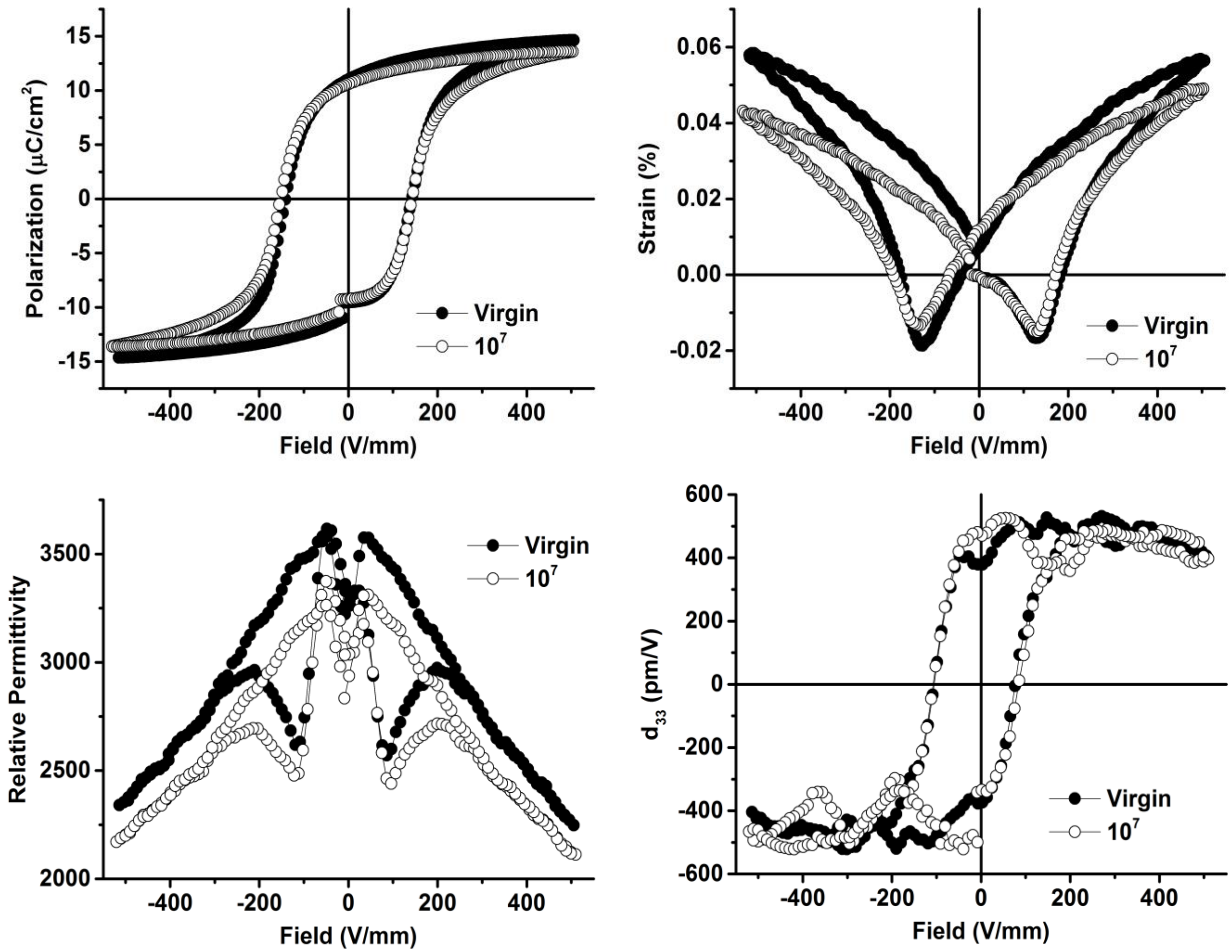




Ehmke et al., *J. Appl. Phys.*, **2012**, *112*, 114108

BCZT
Bipolar fatigue

$BC_{15}TZ_{10}$



<u>Bipolar fatigue</u>

f = 10Hz

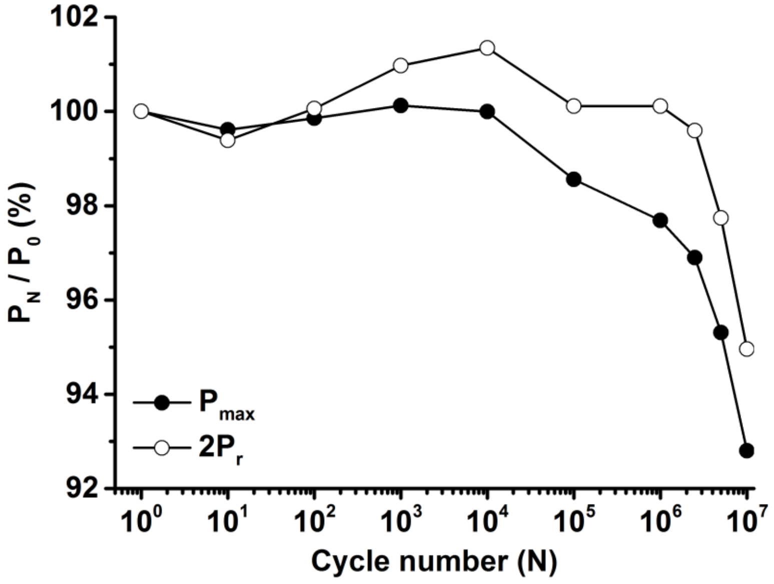
E= 3 E_c

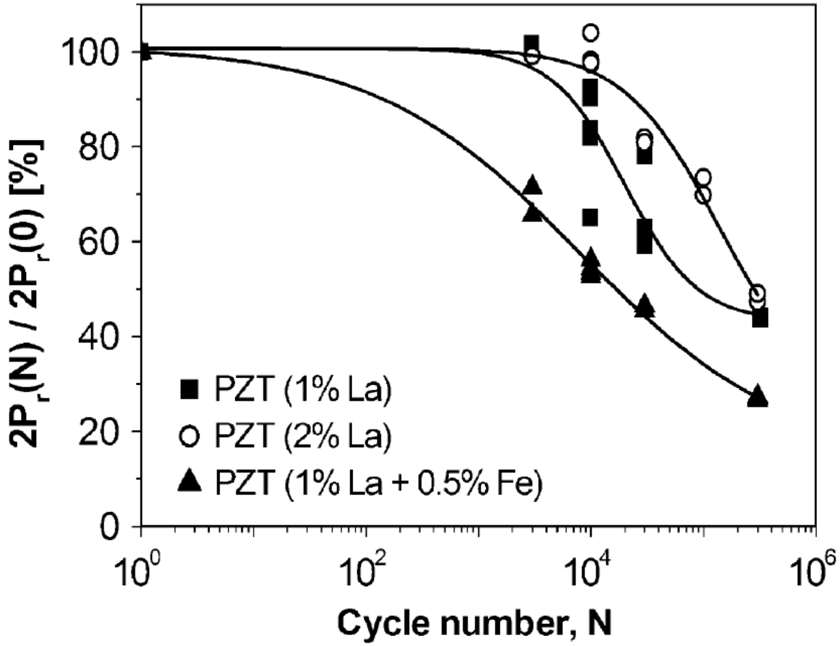
Reduction of

- P_{rem} & P_{max}
- S_{max}
- Permittivity ε_r

BCZT
Bipolar fatigue

Significantly less reduction of polarization compared to soft PZT





BCZT
Cycled bipolar at 10Hz & $3E_c$

Soft PZT
Cycled bipolar at 50Hz and $2E_c$

Balke et al., *J. Amer. Ceram. Soc.*, **2007**, *90*, 3869

BCZT
Unipolar fatigue

Unipolar fatigue

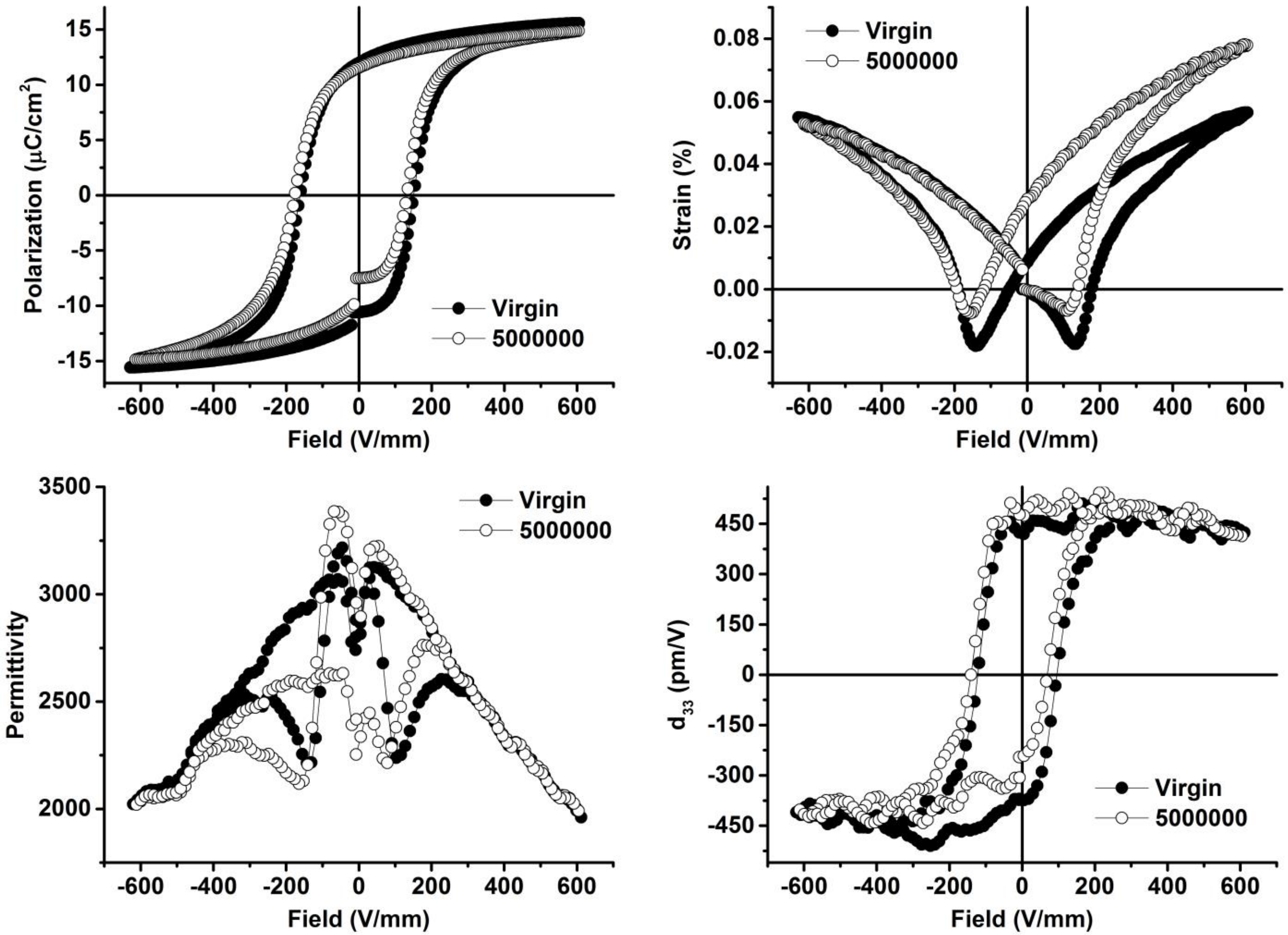
f = 10Hz

E= 3 E_c

Reduction of
- P_{rem} & P_{max}

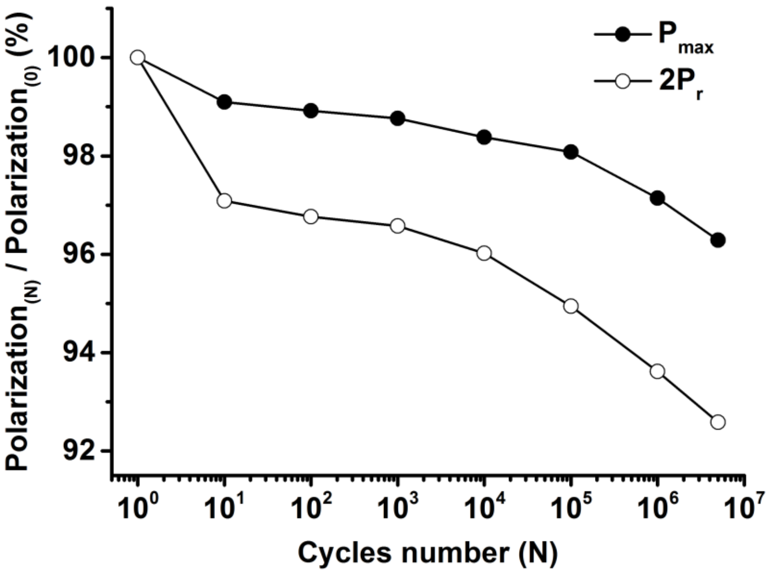
Asymmetries in
- Strain
- Permittivity ε_r

Offset in d_{33}



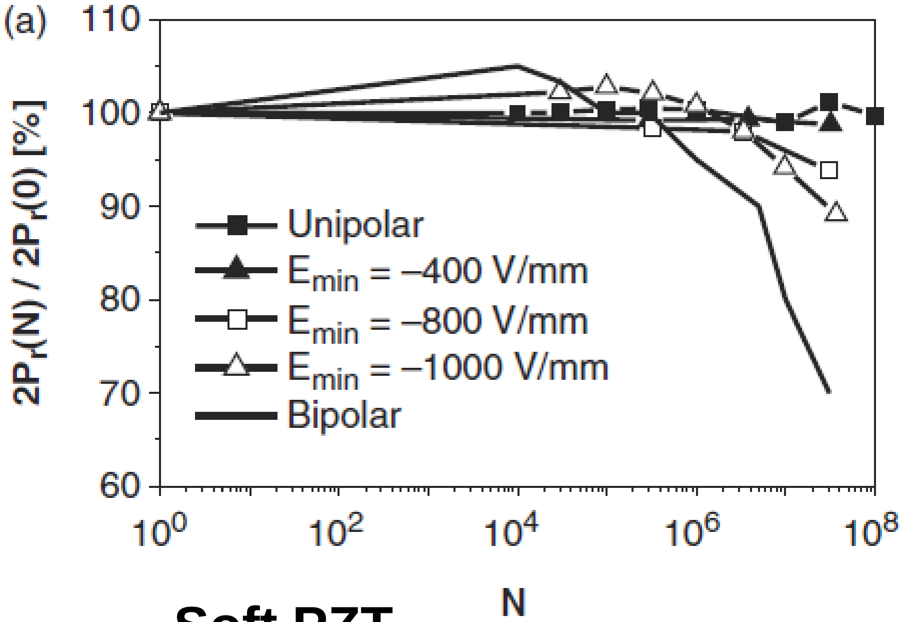
BCZT
Unipolar fatigue

Slightly stronger polarization degradation compared to soft PZT



BCZT

Unipolar cycling, 10 Hz, $3E_c$



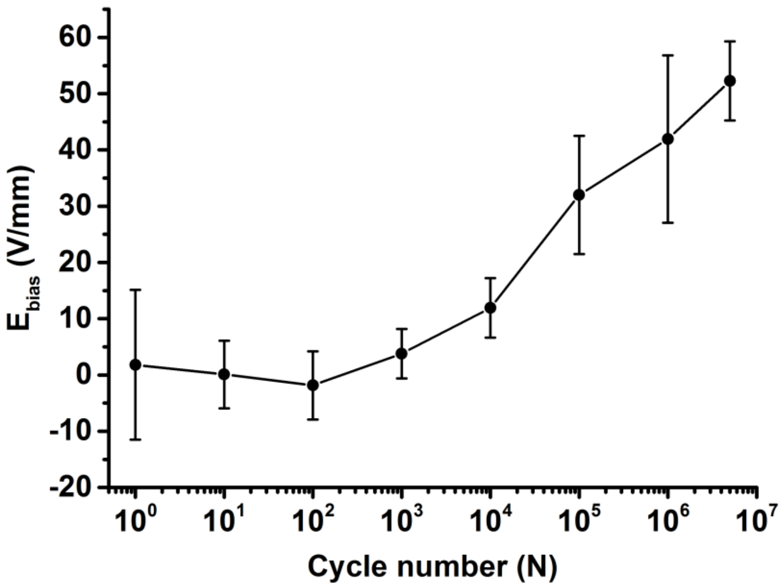
Soft PZT

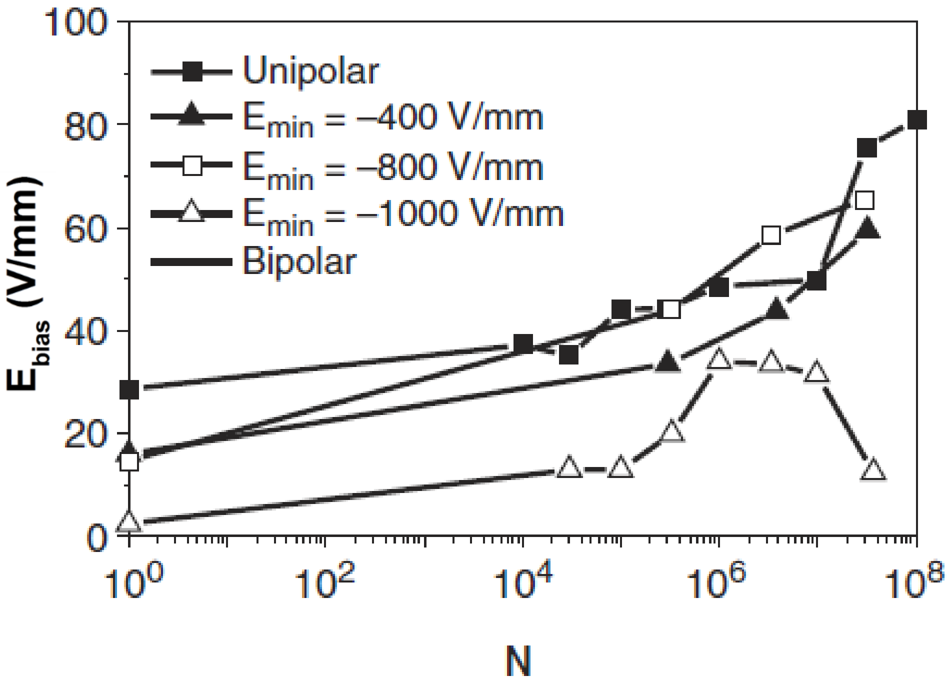
Unipolar cycling, 50 Hz, $2E_c$

Balke et al., *J. Amer. Ceram. Soc.*, **2007**, *90*, 1088

BCZT
Unipolar fatigue

Comparable development of the internal bias field E_{bias}



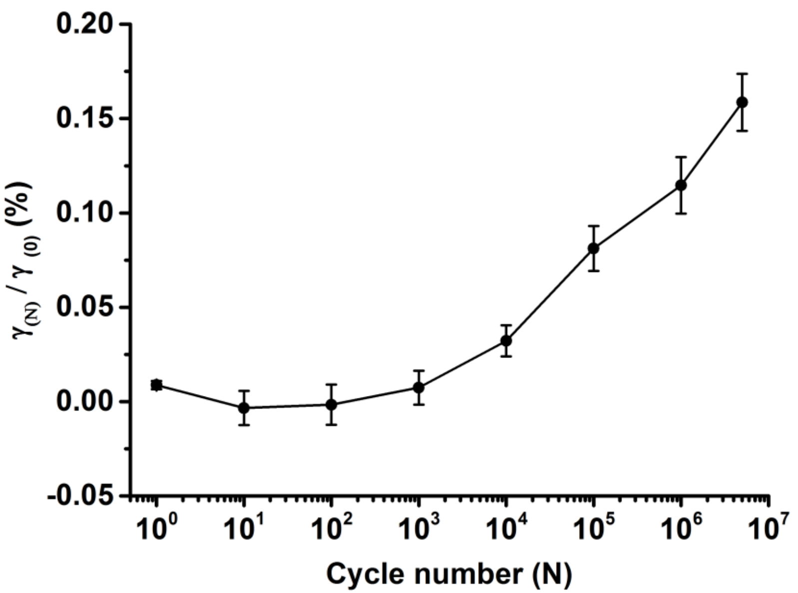


BCZT
Unipolar cycling, 10 Hz, $3E_c$

Soft PZT
Unipolar cycling, 50 Hz, $2E_c$
Balke et al., *J. Amer. Ceram. Soc.*, **2007**, *90*, 1088

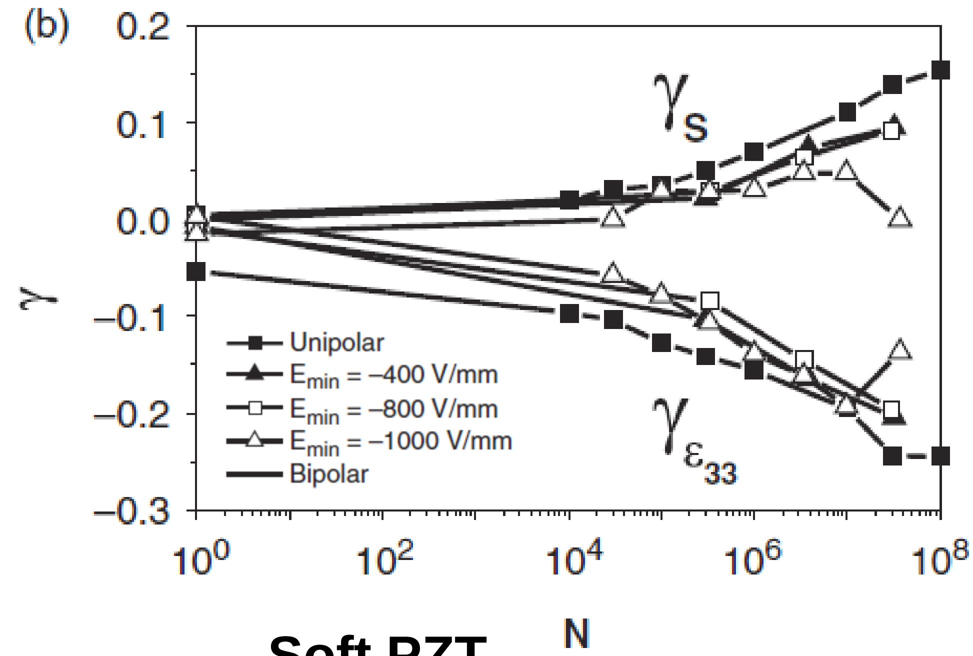
BCZT
Unipolar fatigue

Similar strain asymmetry compared to soft PZT



BCZT

Unipolar cycling, 10 Hz, $3E_c$



Soft PZT

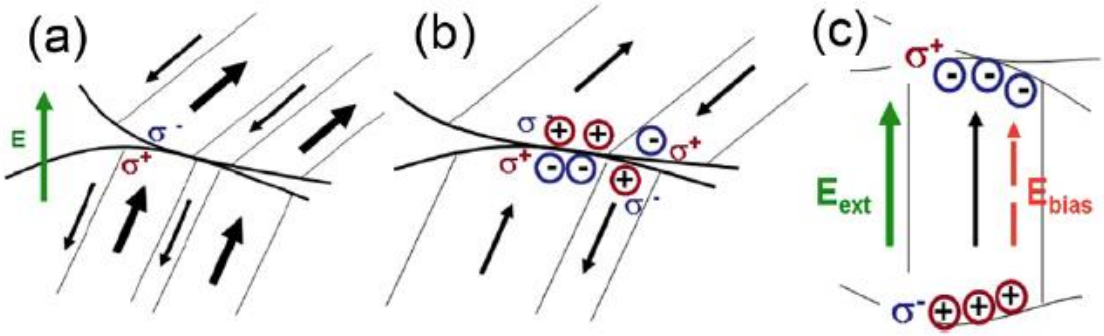
Unipolar cycling, 50 Hz, $2E_c$

Balke et al., *J. Amer. Ceram. Soc.*, **2007**, *90*, 1088

BCZT
Fatigue mechanism

Unipolar fatigue

- Characteristics comparable to soft PZT
- Explainable by charge carrier accumulation



Bipolar fatigue

- In contrast to PZT only slight polarization degradation is observed
- No mechanical degradation observed
- If domain wall pinning occurs, it is only a weak effect

Summary

- Cyclic fatigue behaviour of lead-free piezoceramics elucidated: BNT-BT; BNT-KNN-BT; BCZT
- Cyclic fatigue degradation occurs in lead-free piezoceramics
- Dependence upon the electric field – temperature phase diagram
- Mechanisms:
  - Domain wall pinning
  - Domain fragmentation
  - Domain structure vanishes ($T>T_0$)

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