Developing Lead-Free Piezoceramics

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Outline

Ferroelectrics: starting projects – 2003
5 projects ended

Synthesis

A1
Rödel
Lead-Free

A2
Hoffmann
PZT
ended 2010

Modeling

C1
Albe
Defect Structure

C3
Müller/Becker
ended 2010

C5
Genenko/von Seggern
Charge Transport

Characterization

B1
Eichel/Dinse
ended 2010

B3
Kleebe/Donner
TEM/XRD

B5
Lupascu/Rödel
ended 2006

B2
Balogh
ended 2010

B7
von Seggern/Klein
Polarization Dynamics

Components

D1
Rödel
El. Fatigue

Ferroelectrics: current projects – 2014
4 new projects started

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Synthesis

A1
Rödel
Lead-Free

Modeling

C1
Albe
Defect Structure

C6
Xu
defect /dw interaction
started 2012

C5
Genenko/von Seggern
Charge Transport

Characterization

B3
Kleebe/Donner
TEM/XRD

B9
Buntkowsky
NMR
started 2009

B7
von Seggern/Klein
Polarization Dynamics

Components

T2
Hoffmann
PbO Stoichiometry
started 2011

D6
Webber
Mechanics
started 2012

D1
Rödel
El. Fatigue

Legislation

RoHS II	ELV
Lead-containing piezoelectric devices	Lead-containing piezoelectric devices
Category 7	Category 10 (a)

Exemptions expire latest after maximum validity period

5 years (July 2016)
Categories 1-7,10
→ **Continuous process** →

UNLESS INDUSTRY REQUESTS CONTINUATION!

18 MONTHS PRIOR TO EXPIRY → Next revision for INDUSTRY July 2016

EU-Directive 2000/53/EC: ELV. Off. J. Eur. Un. 2000;L 269:34 //EU-Directive 2011/65/EU: RoHS II. Off. J. Eur. Un. 2011;L 174:88

History of lead-free piezoceramics

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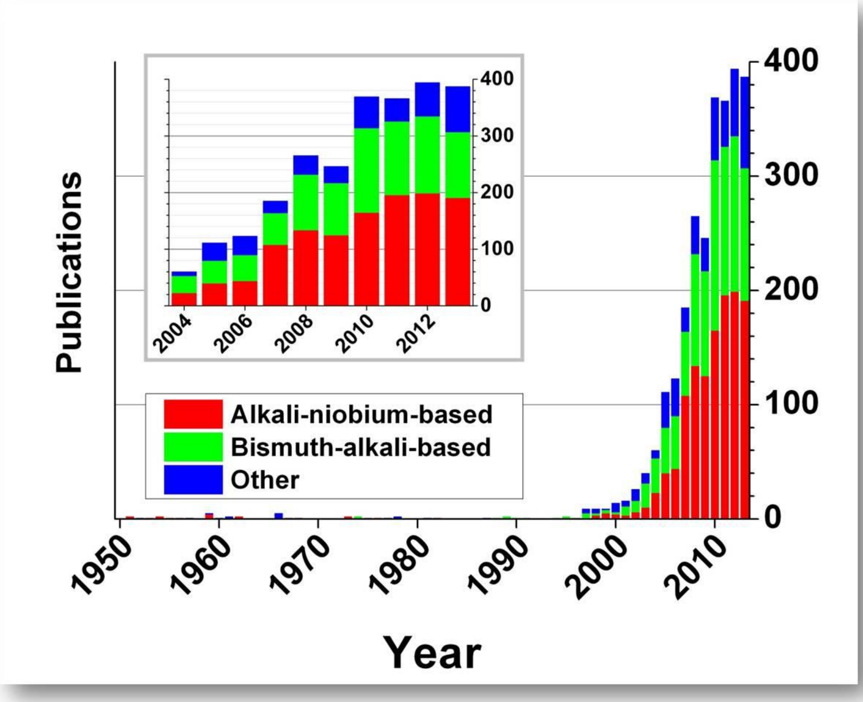
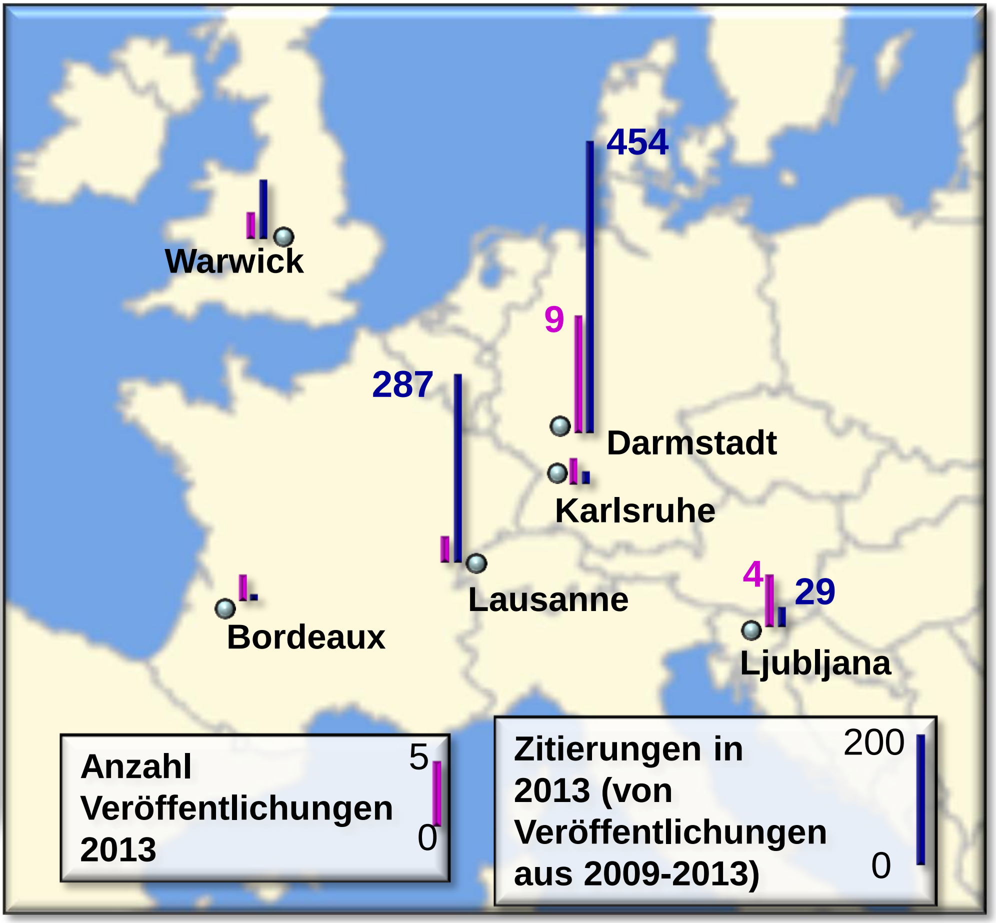
KNN-based	BNT-based	Other
1954 1st report KNN (Shirane et al.)		**1945** $BaTiO_3$ piezo transducer (patent)
		1945 Poling process (Gray)
1959 Piezoelectric data of KNN (Egerton&Dillon)	**1957** BKT discovery (Popper et al.)	**mid 1950s** PZT ceramics
	1960 BKT properties (Smolenskii et al.)	
	1991 BNT-BT (Takenaka et al.)	
	1996 BNT-BKT (Elkechai et al.)	**2001** EU LEAF project
2004 LF4 composition (Saito et al.)	**2007** BNT-BT-KNN (Zhang et al.)	**2003** 1st EU legislative
2004 Improving the sintering, e.g. Cu-doping (Matsubara et al.)		
2013 Temperature-insensitive strain in KNN (Wang et al.)	**2009** hard BNT-BT for ultrasonic cleaners (Tou et al.)	**2009** BCT-BZT (Liu, Ren)
2014 KNN+ Ni electrodes (Liu et al.)	**2014** Mn- and Fe-doped BNT-BKT-BLT (Taghaddos et al.)	**2014** BCT-BZT high d_{33}* (Ehmke et al.)

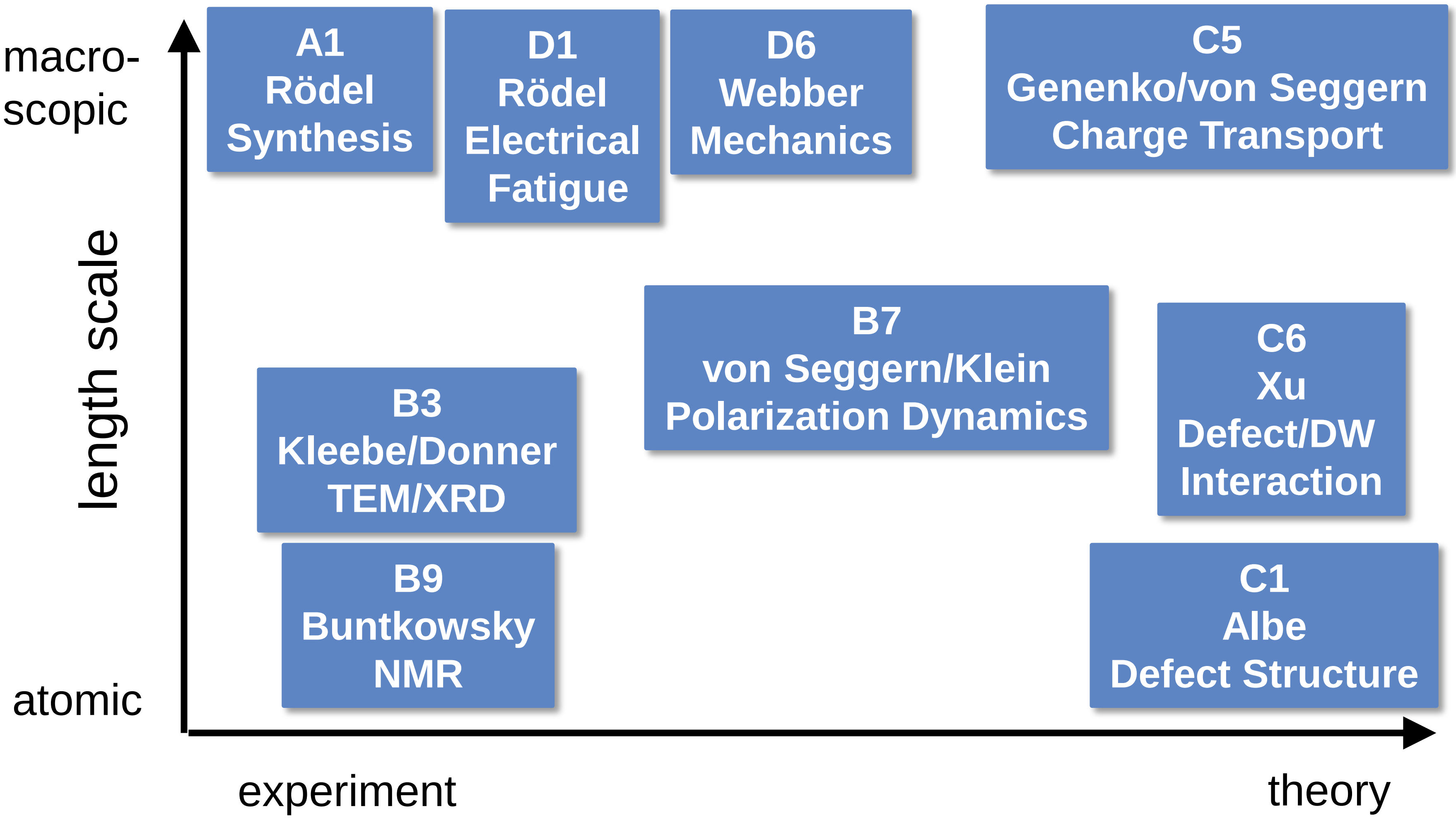
Publications on lead-free piezoceramics





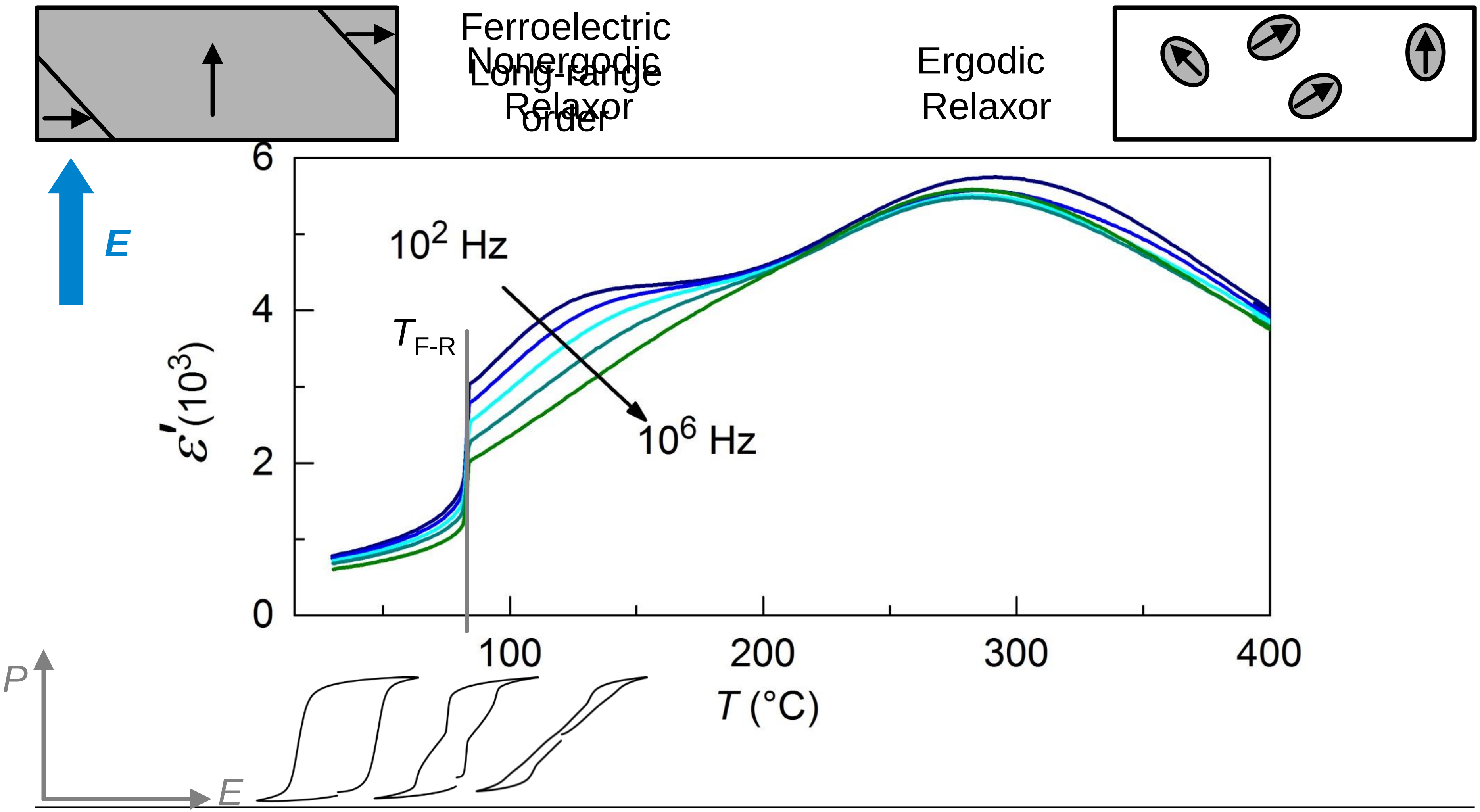
BNT-based

BNT-based piezoceramics - projects



P(E,T) in BNT-6BT

D1



E-T Diagram in BNT-3BT:Mn

D1

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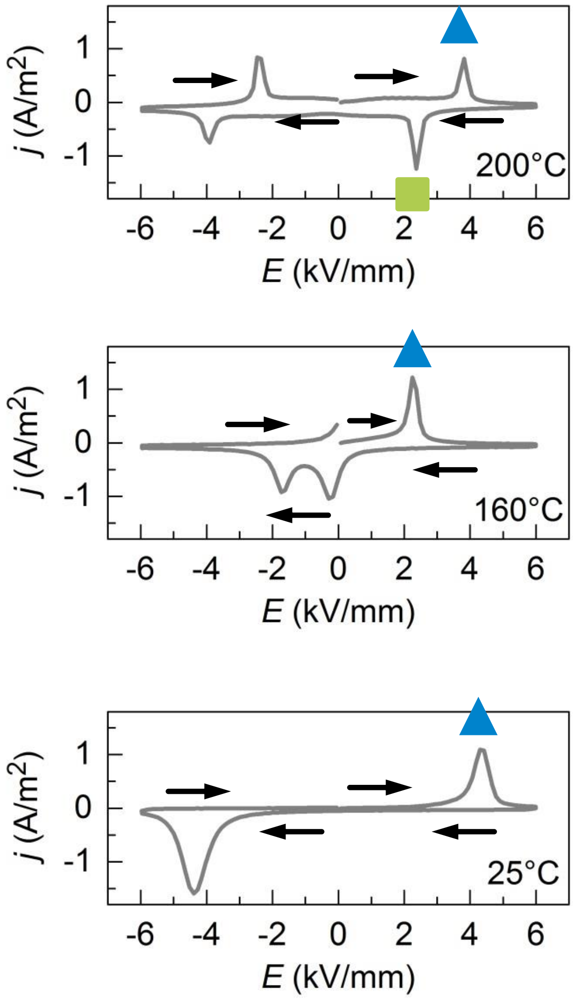

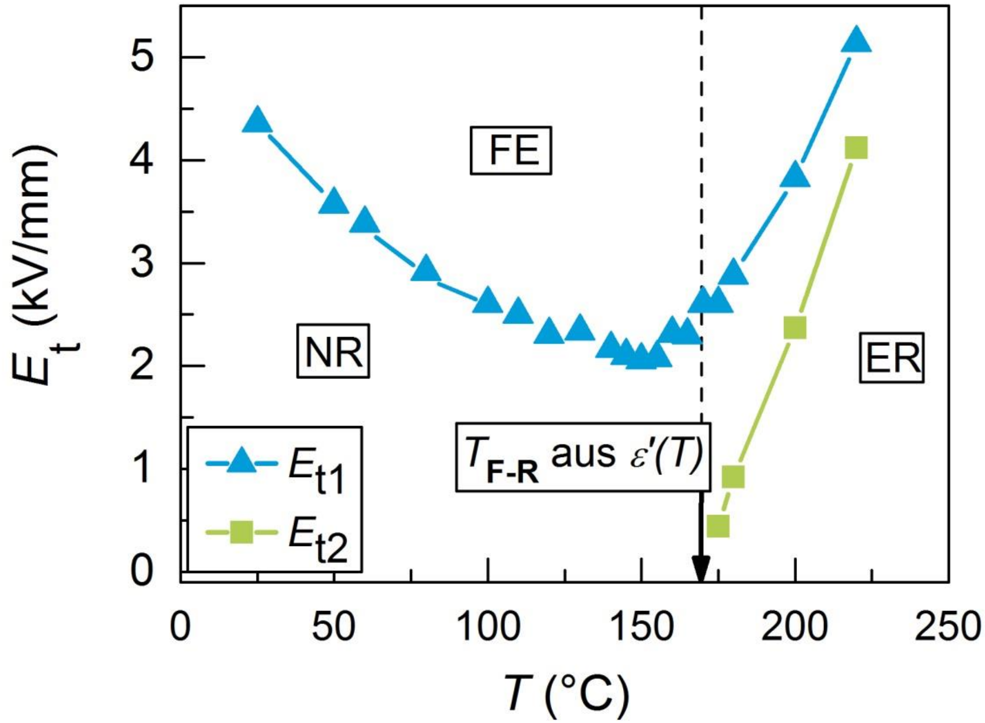

Sapper *et al.*, J. Appl. Phys. 115, 194104 (2014)

Fe-modification=hard-doping?

D1

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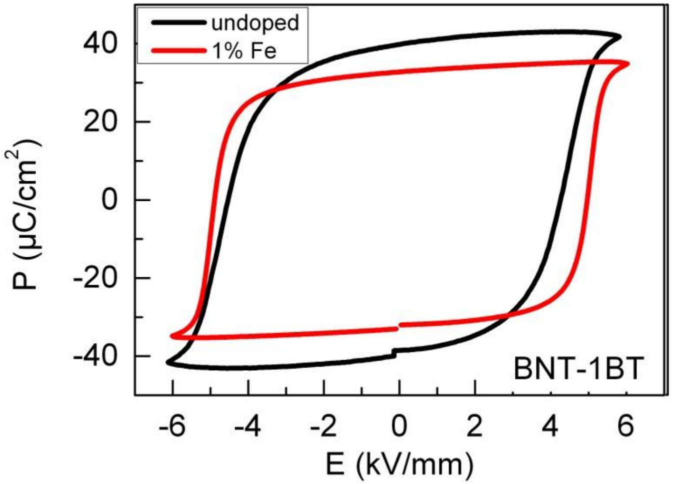
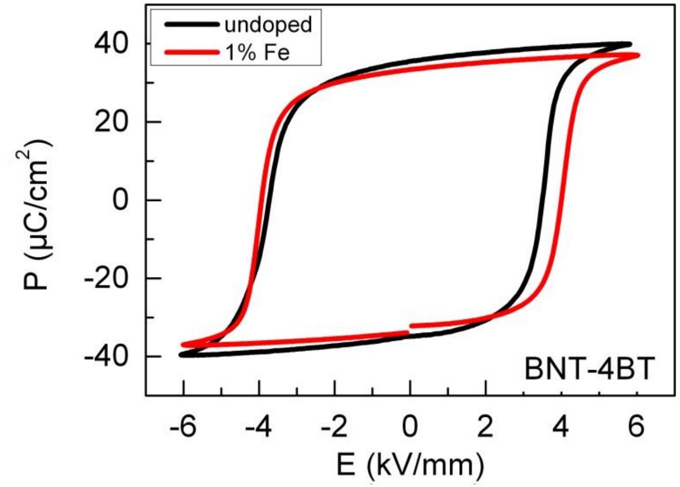
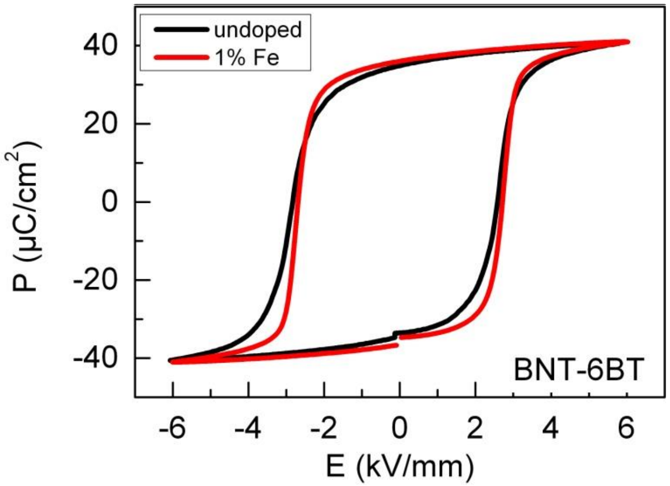
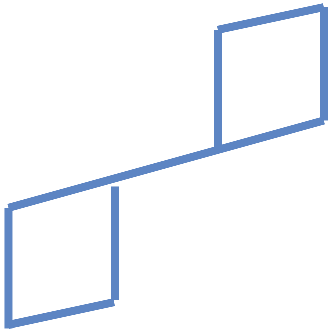


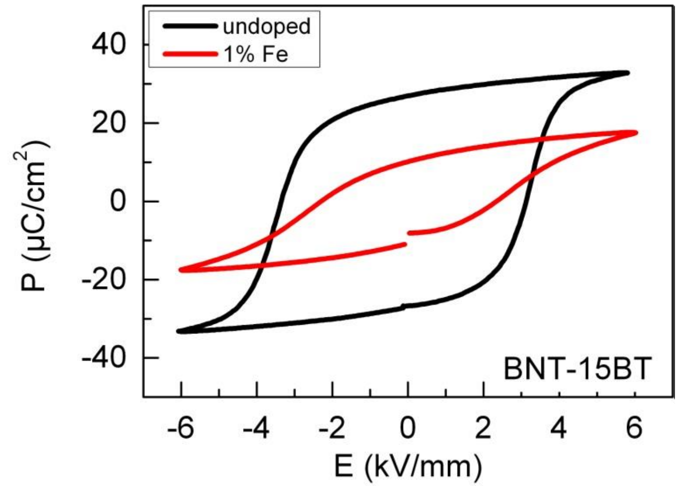
expectation:
E_{bias} up
P_r down
strongly aged:
pinched loop





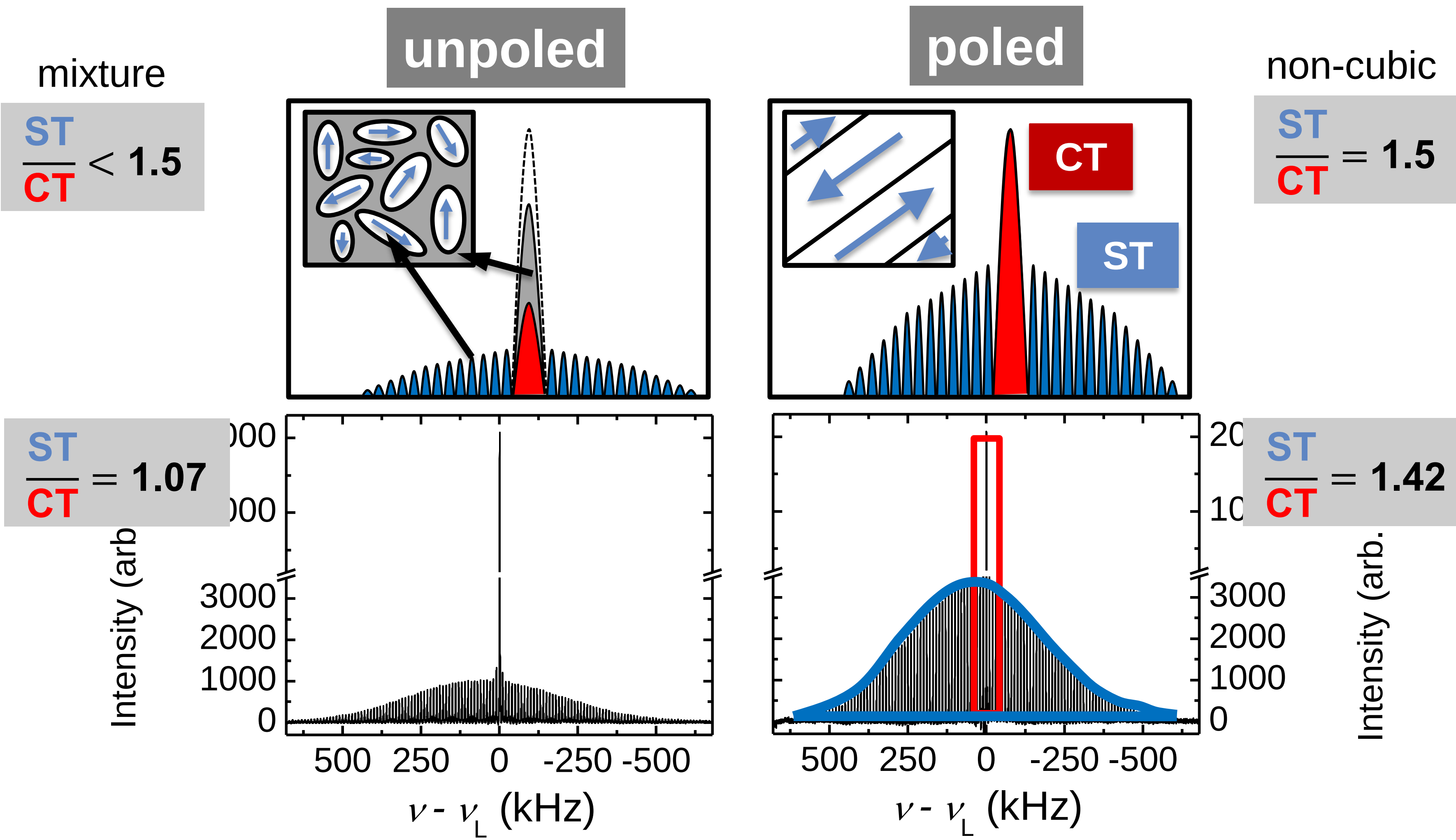


measurement



^{23}Na MAS NMR –
Local structure of BNT-6BT

B9



Pedro Braga-Groszewicz, submitted to PRL

Atomic Structure of BNT

C1

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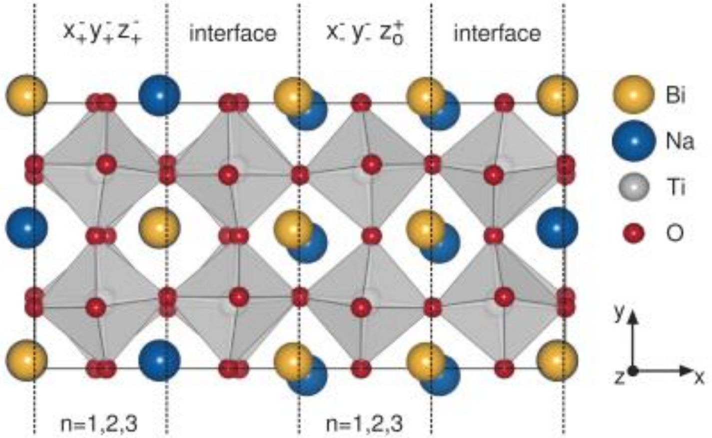

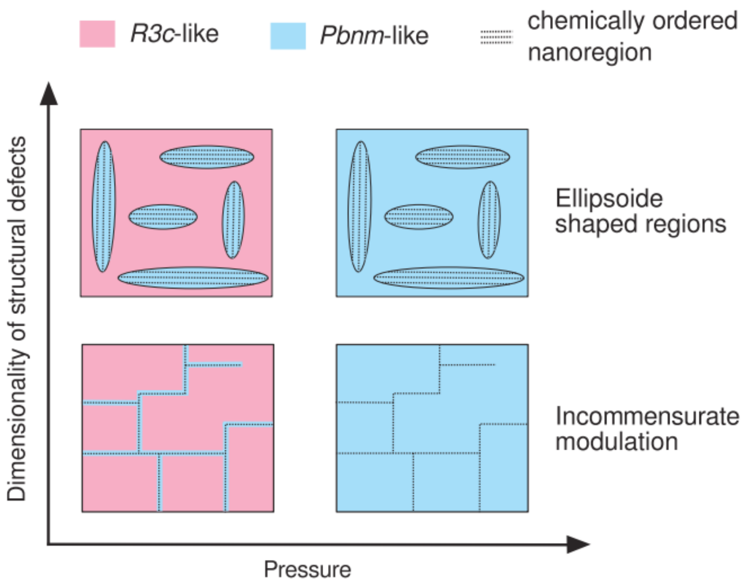

- Zero pressure: BNT is structurally frustrated
- Ab initio calculations suggest the existence of chemically ordered nanoregions (CNR)
- Matrix: *R3c*-like CNR: *Pbnm*-like

Gröting *et al.*, Phys. Rev. B. 86, 134118 (2012)

Diffuse scattering BNT-4BT single crystal

B3

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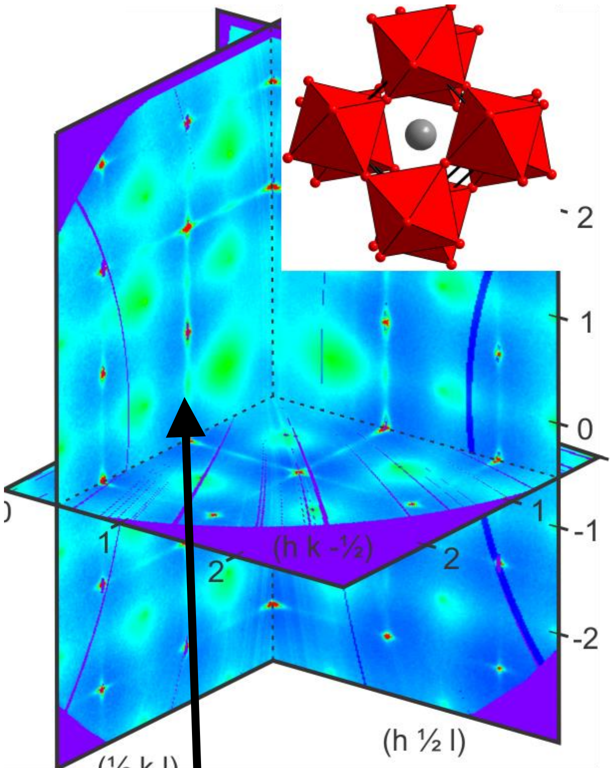
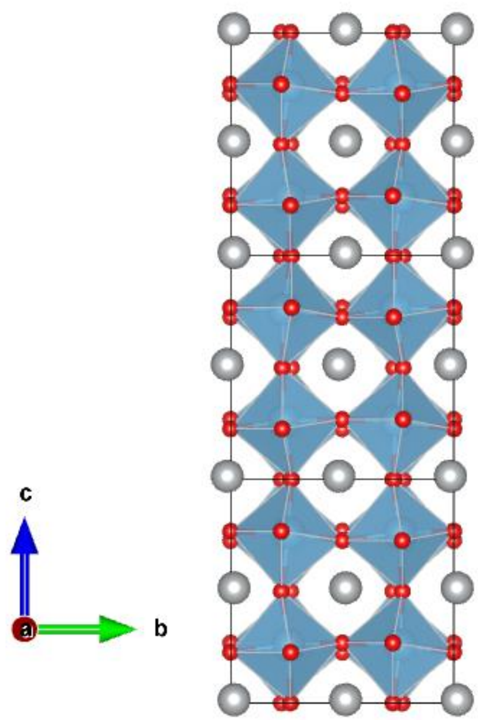
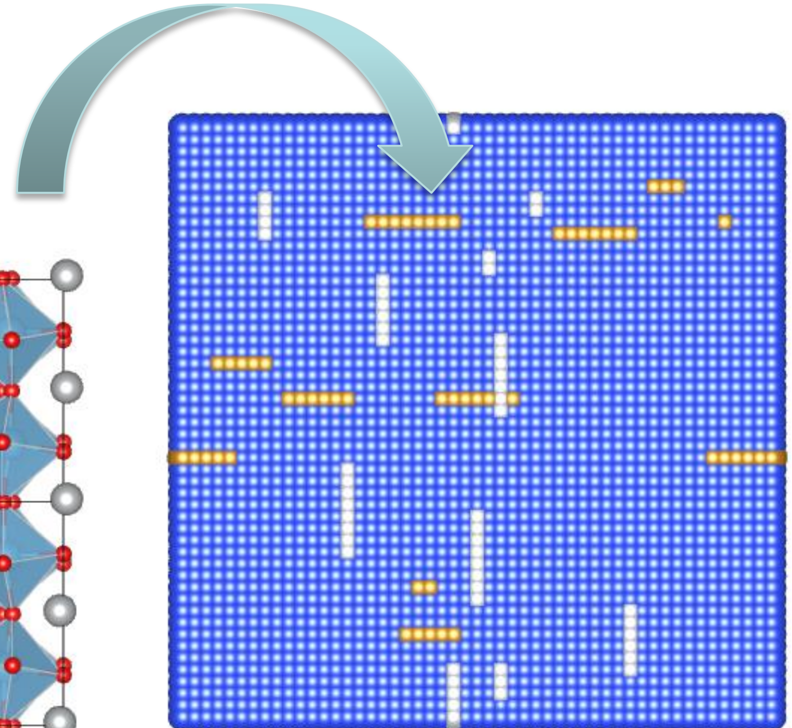


Streaks
→ Random Stacking Faults

Defect:
Stacking Fault
in Tilt Sequence





Stacking Faults are the Boundaries of PNRs

Streaks: Daniels *et al.*, Appl. Phys. Lett. 98, 252904 (2011)

TEM as *f(T)* in BNT-6BT-1KNN

A1, B3

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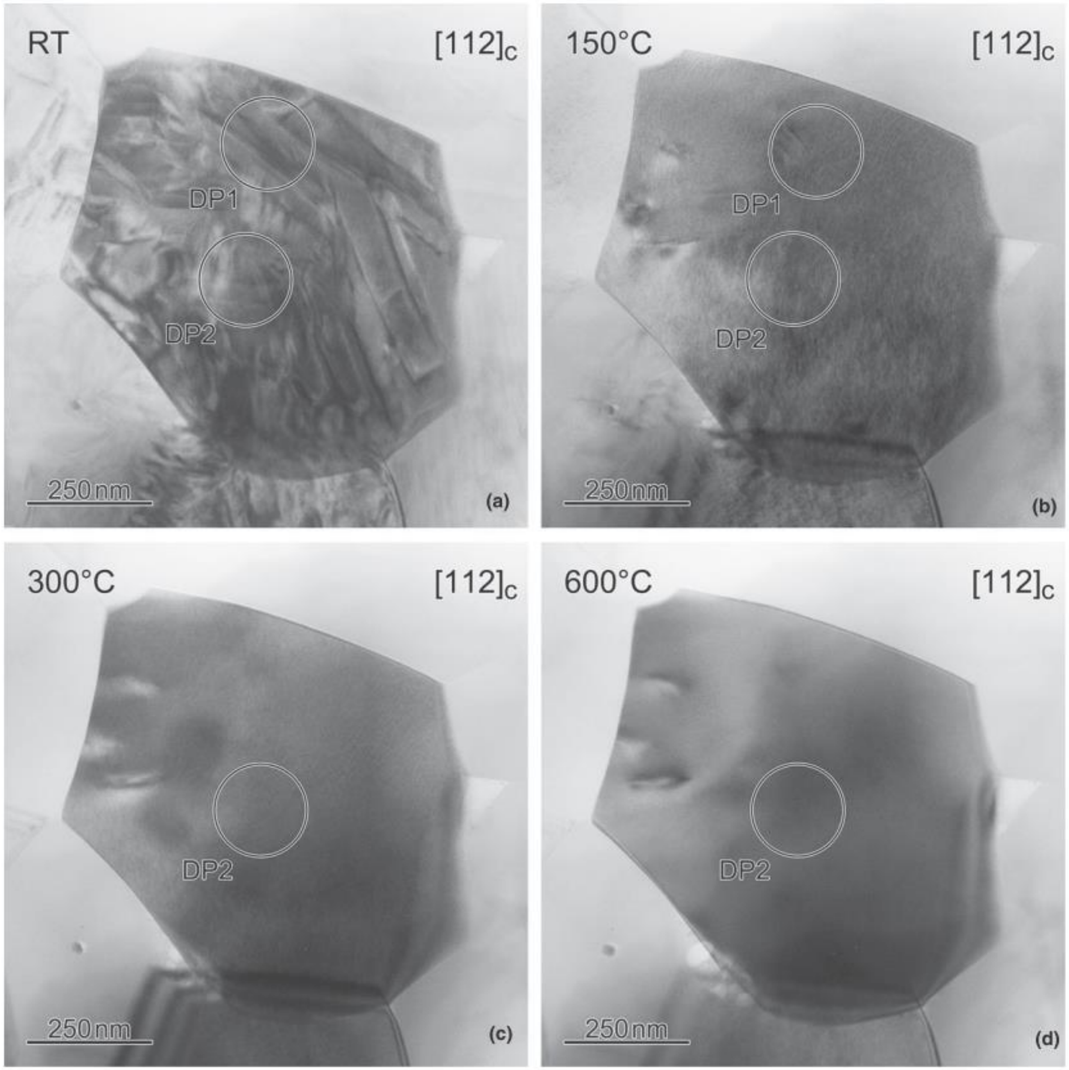

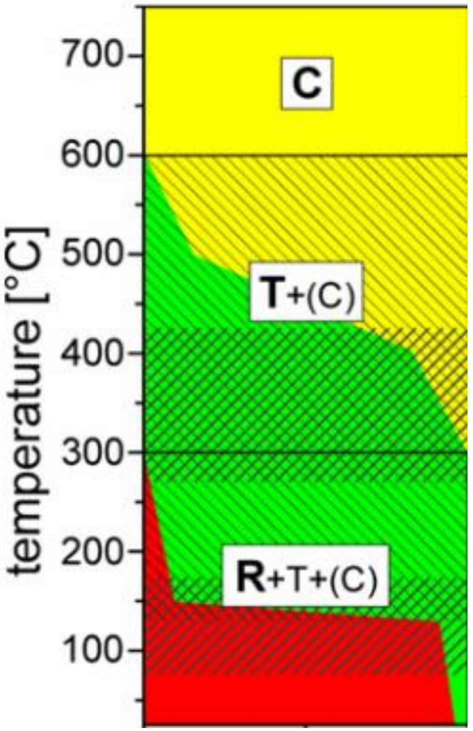

94BNT-5BT-1KNN

Kling *et al.*, J. Am. Ceram. Soc. 96, 3312 (2013)

Phase transitions in BNT-6BT: *f(σ)*

A1,(D6)

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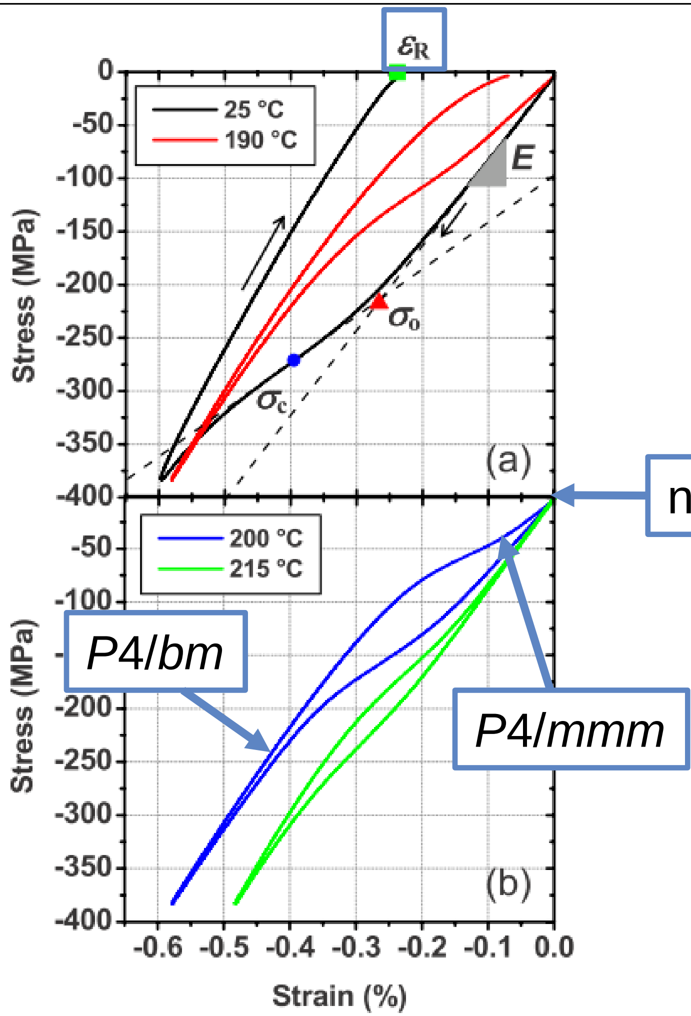

- Stress-free XRD:
polar tetragonal *P4mm* to non-polar tetragonal *P4/mmm* at 195°C

no remanent strain

- Uniaxial compressive stress:
Field-induced *P4/mmm to P4/bm*
→oxygen octahedral tilting
→stress induced phase transition

Webber *et al*., J. Appl. Phys. 108, 014101 (2010)

BNT-based actuator materials

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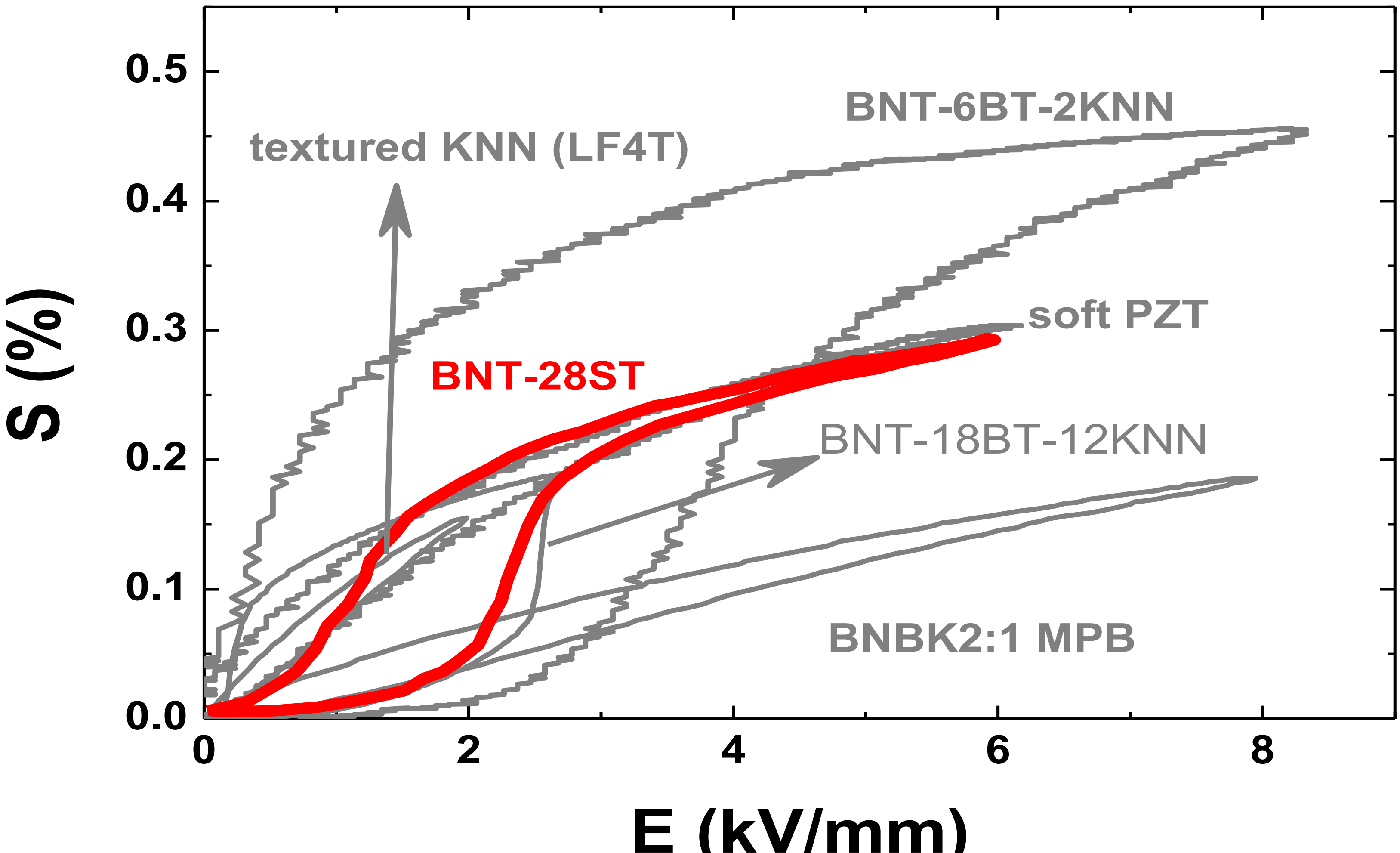

Jo *et al*., J. Electroceram. 29, 71-93 (2012)

Relaxor Ferroelectric Composites

A1, C. Groh associated

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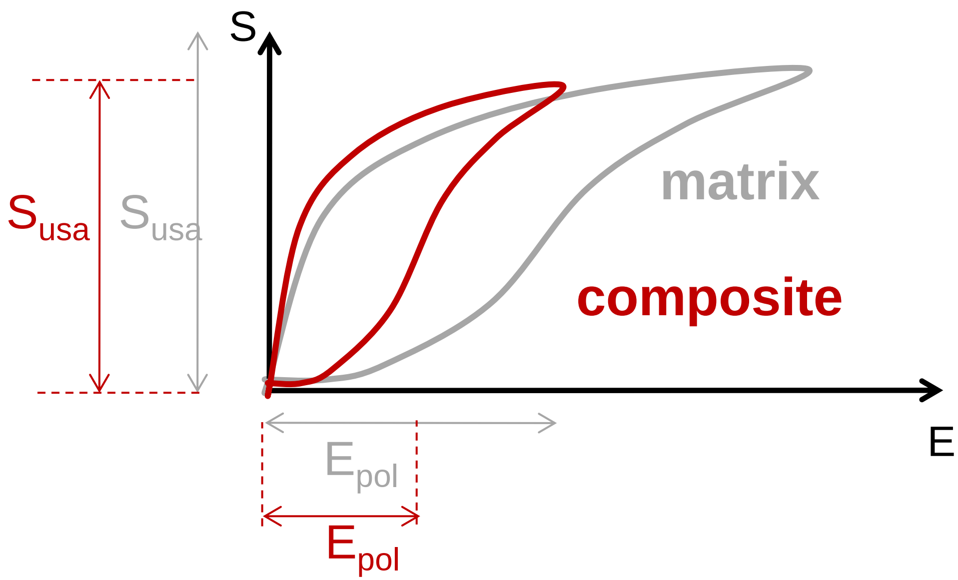

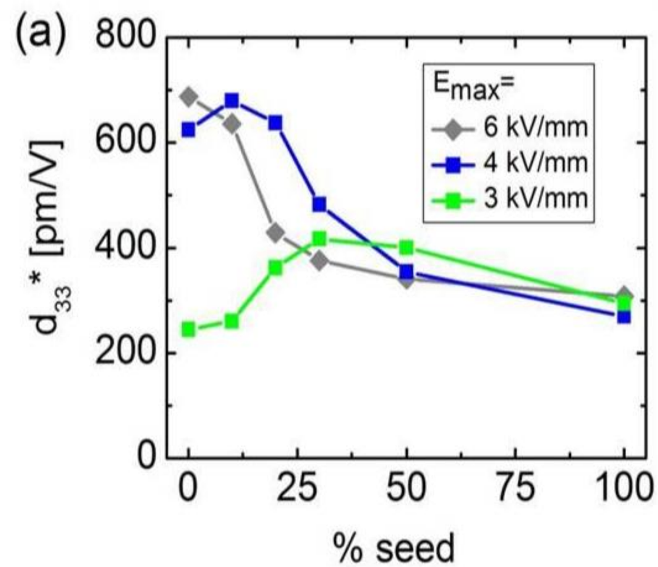

Mechanism:

- Electric field → seed gets poled first → propagates polarization to matrix → core gets "easier" poled ≙ polarization at lower fields (E_{pol} ↓)
- Only small amounts of shell required (nuclei of polarization) → maintain the high strain of matrix

Groh *et al*., Adv. Funct. Mat. 24, 336-362 (2014)

Coupling mechanisms

A1, C. Groh
Haibo Zhang (AvH)

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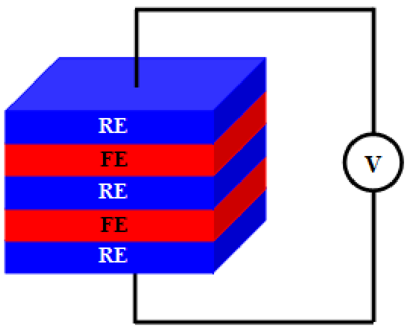
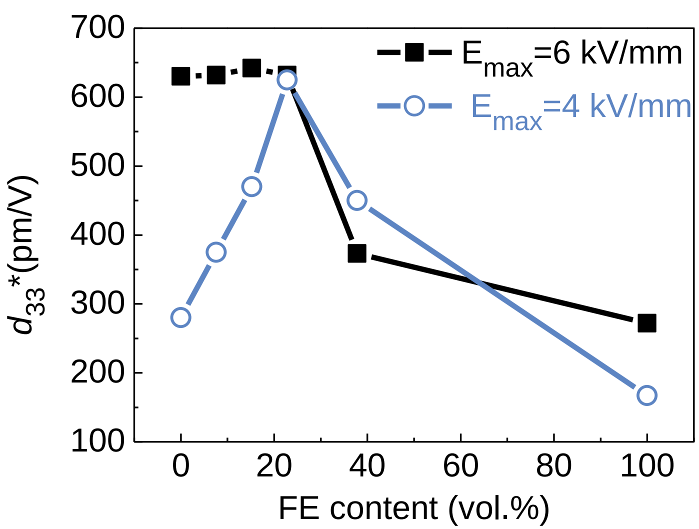
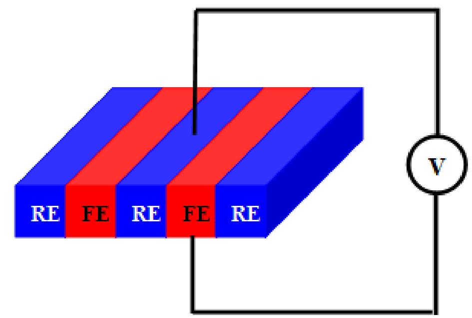
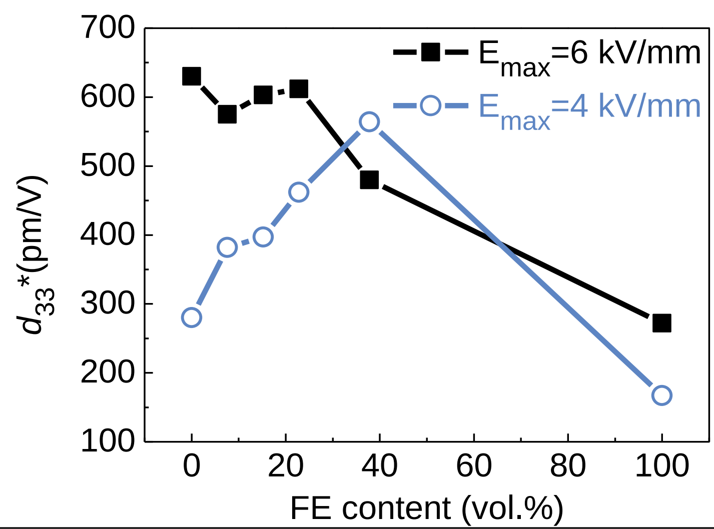
Polarization coupling





Strain coupling





BZT-BCT

$Ba(Zr_{0.2}Ti_{0.8})O_3$-$x(Ba_{0.7}Ca_{0.3})TiO_3$

A1, M. Acosta associated

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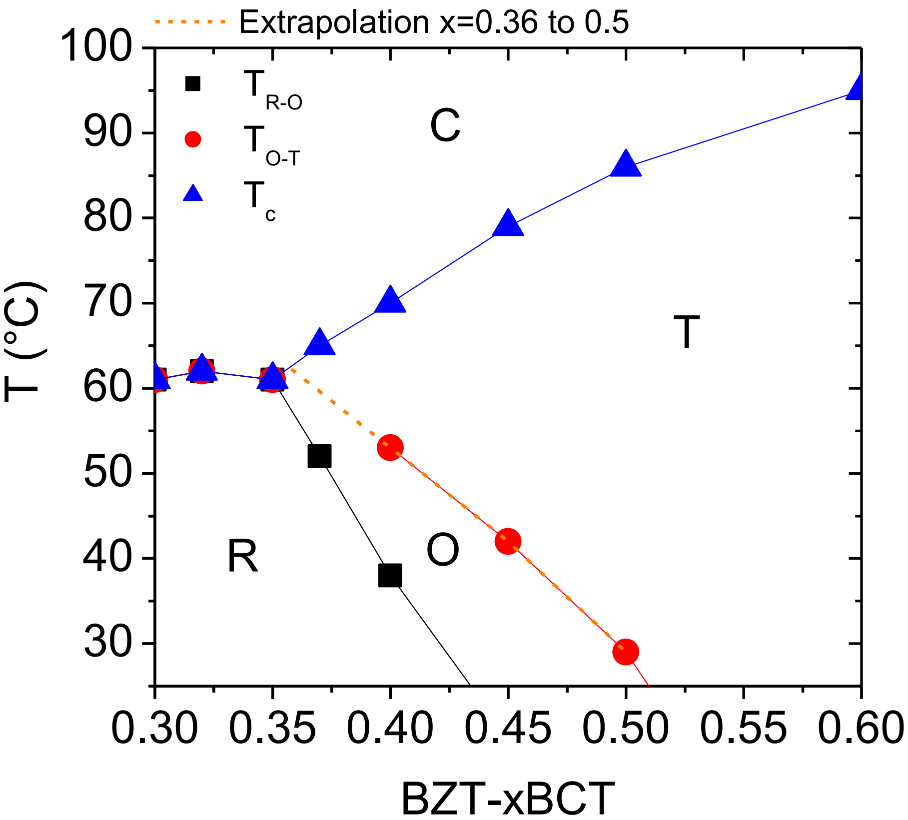
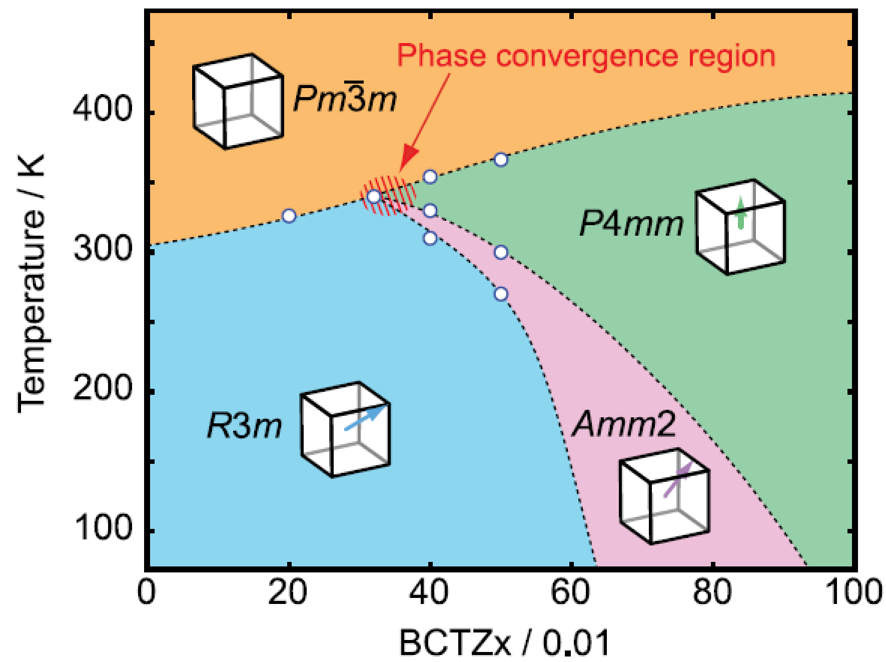


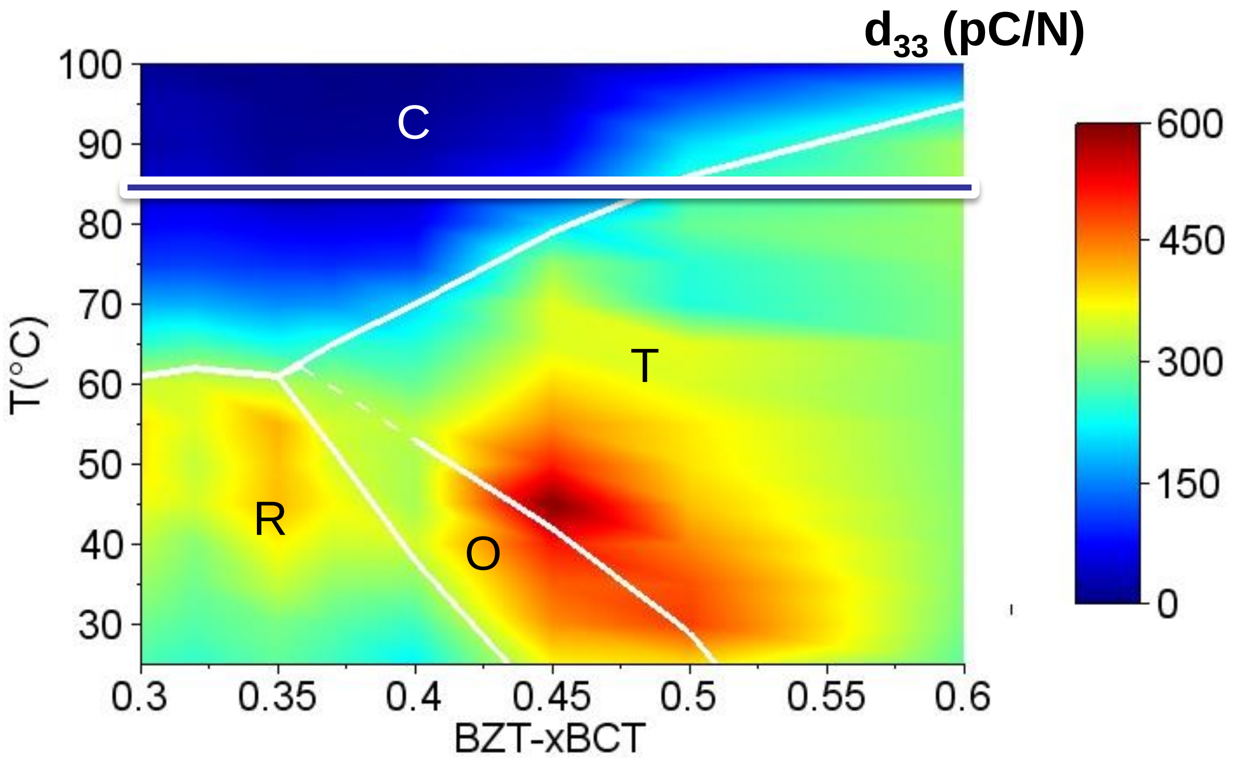


Acosta *et al*., Acta Mater. 80, 48-55 (2014)

Keeble *et al*., Appl. Phys. Lett. 102, 092903 (2013)

BZT-xBCT: small signal d_{33} as f(x, T)

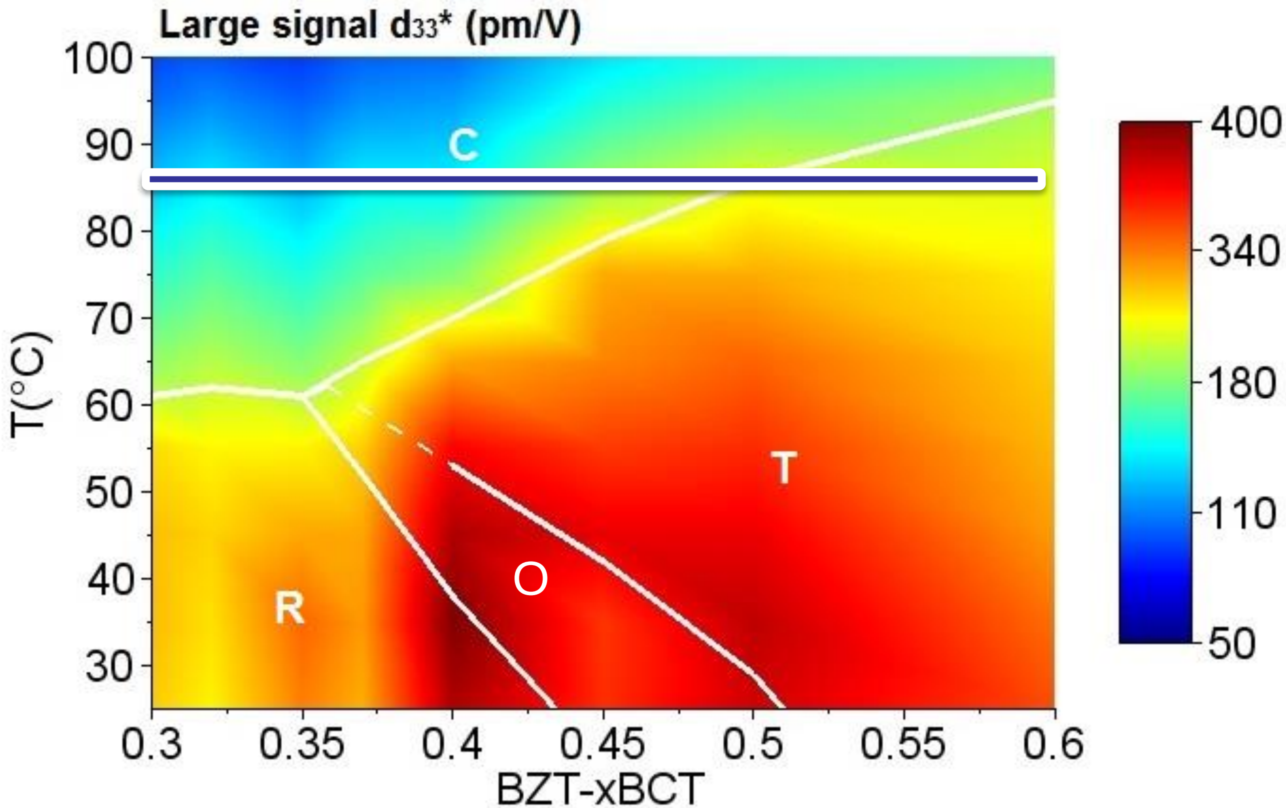
A1, M. Acosta associated



- Peak at O-T phase transition
- No peaking at triple points
- Applications limited below 95 °C at x=0.6 → d_{33}~300 pC/N

Acosta *et al*., Acta Mater. 80, 48-55 (2014)

BZT-xBCT: large signal d_{33}^* as f(x, T)



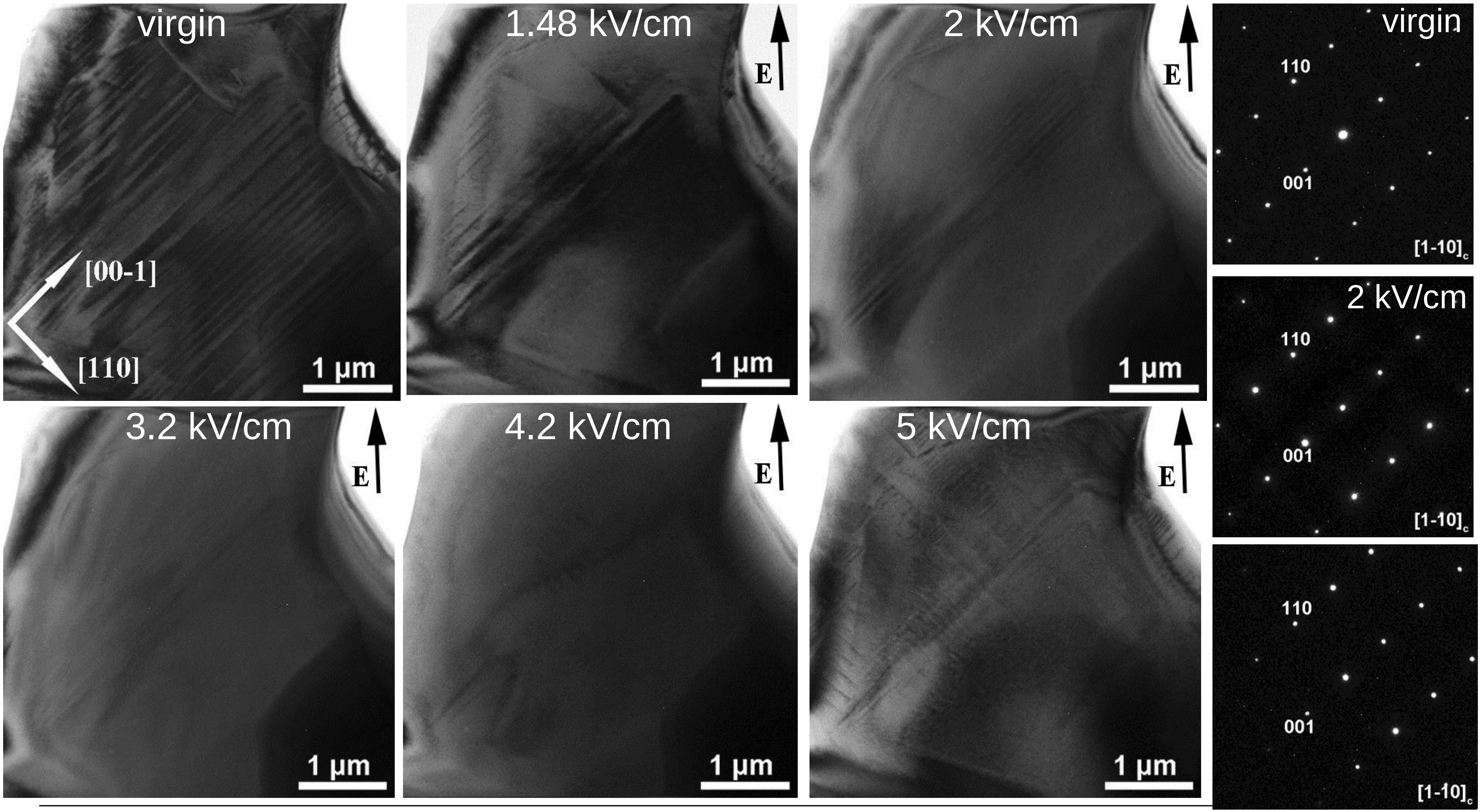
A1, M. Acosta associated

- Peak at R-O and O-T phase transitions
- No peaking at convergence region!
- Low temperature stability limits applications below 90 °C

Acosta *et al*., Acta Mater. 80, 48-55 (2014)

In-situ E-field studies
BZT-0.32BCT

A1, M. Acosta, B3
X. Tan (Iowa State Univ., USA)



H.Guo, X.Tan, Iowa State University, USA

Polarization dynamics in BZT-xBCT

A1, M. Acosta
B7, S. Zhukov

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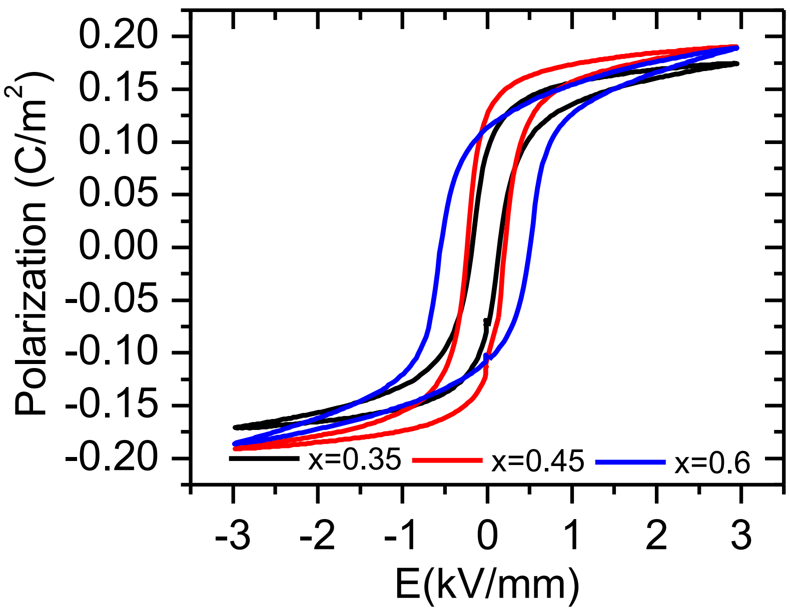

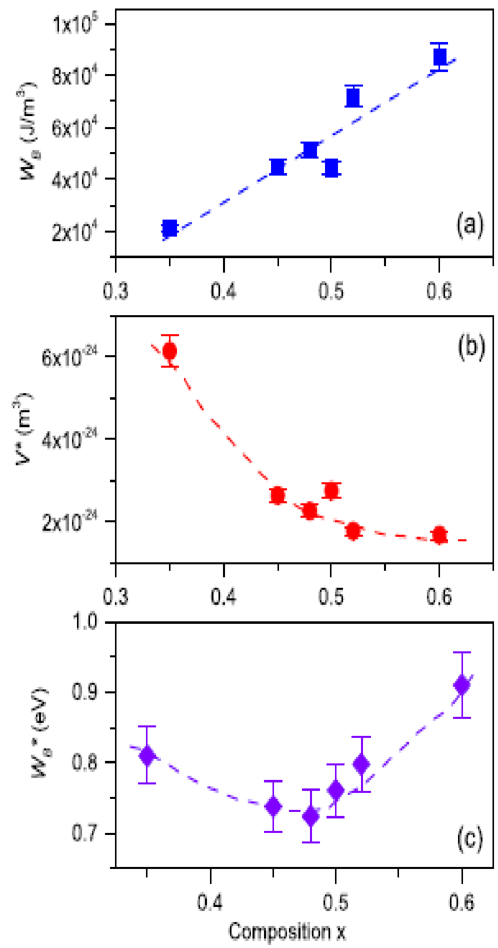

Thermodynamic activation barrier per unit of volume

Critical volume of nucleating domain

Activation barrier

$$W_B^* = W_B \times V^*$$

- Maximized properties due to minimum in activation barrier for domain switching

Zhukov *et al.* Appl. Phys. Lett. 103, 152904 (2013)

BZT-BCT under uniaxial compressive stress

A1, M. Ehmke
Purdue Univ., USA

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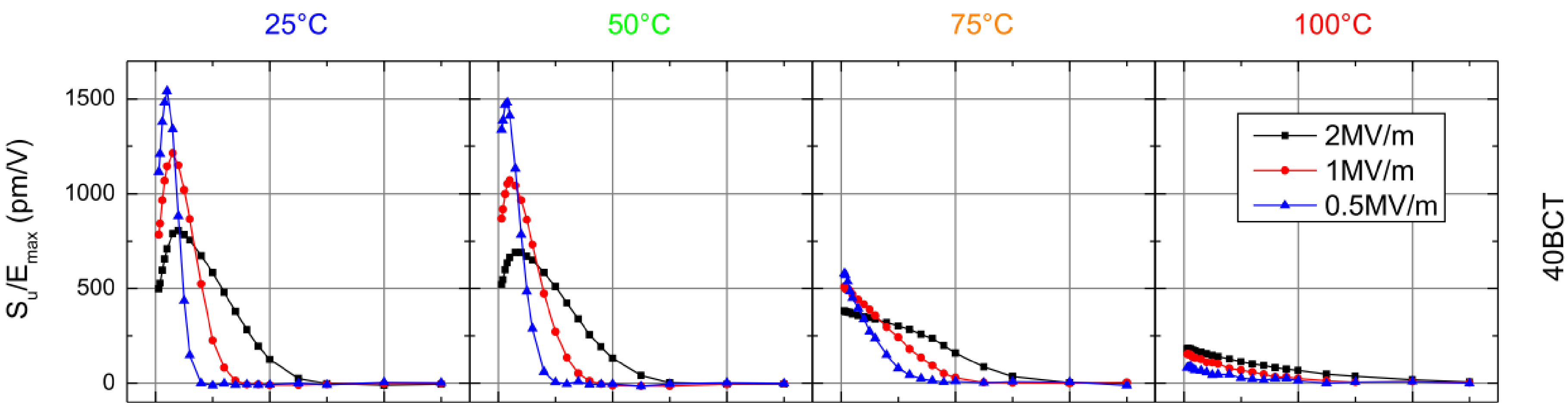


<u>BNT-40BCT</u>

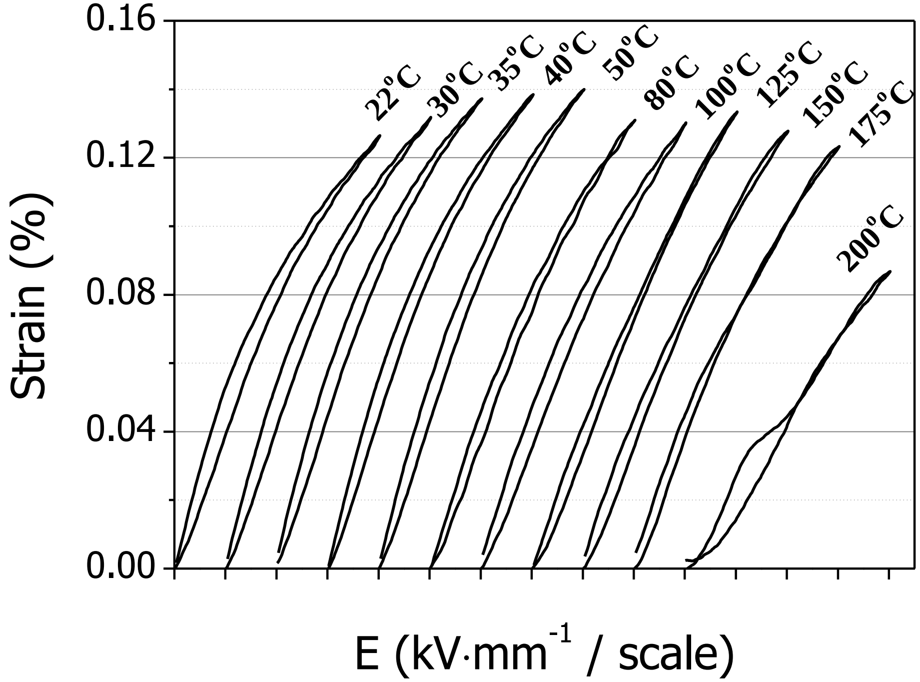
- Stress < 50 MPa increasing d_{33}* at low E and T
- Mechanical loading: *E* stabilizes domains parallel to stress
- Moderate stresses: favour strain

  → *E* is large enough to reorient ferroelastically switched domains

M. Ehmke *et al.*, Acta Mater. 78, 37-45 (2014)

KNN-based

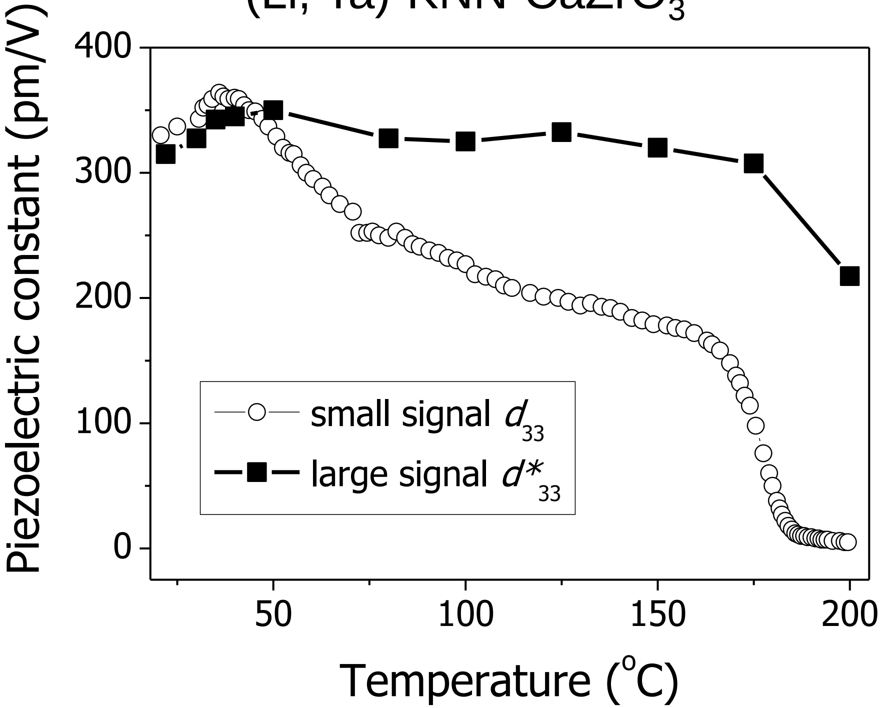
Temperature-Insensitive Strain in modified KNN



Ke Wang (AvH fellow)
Tsinghua Univ., China

@4kV/mm

(Li, Ta)-KNN-$CaZrO_3$



$$S=Q(P_{max}^2-P_r^2)$$

300pm/V < d_{33}* < 350pm/V
from RT to 175°C

Ke Wang *et al.*, Adv. Funct. Mater. 23, 4079-86 (2013)

MPB in KNN-based ceramics

Ruiping Wang
(AIST, Tsukuba, Japan)

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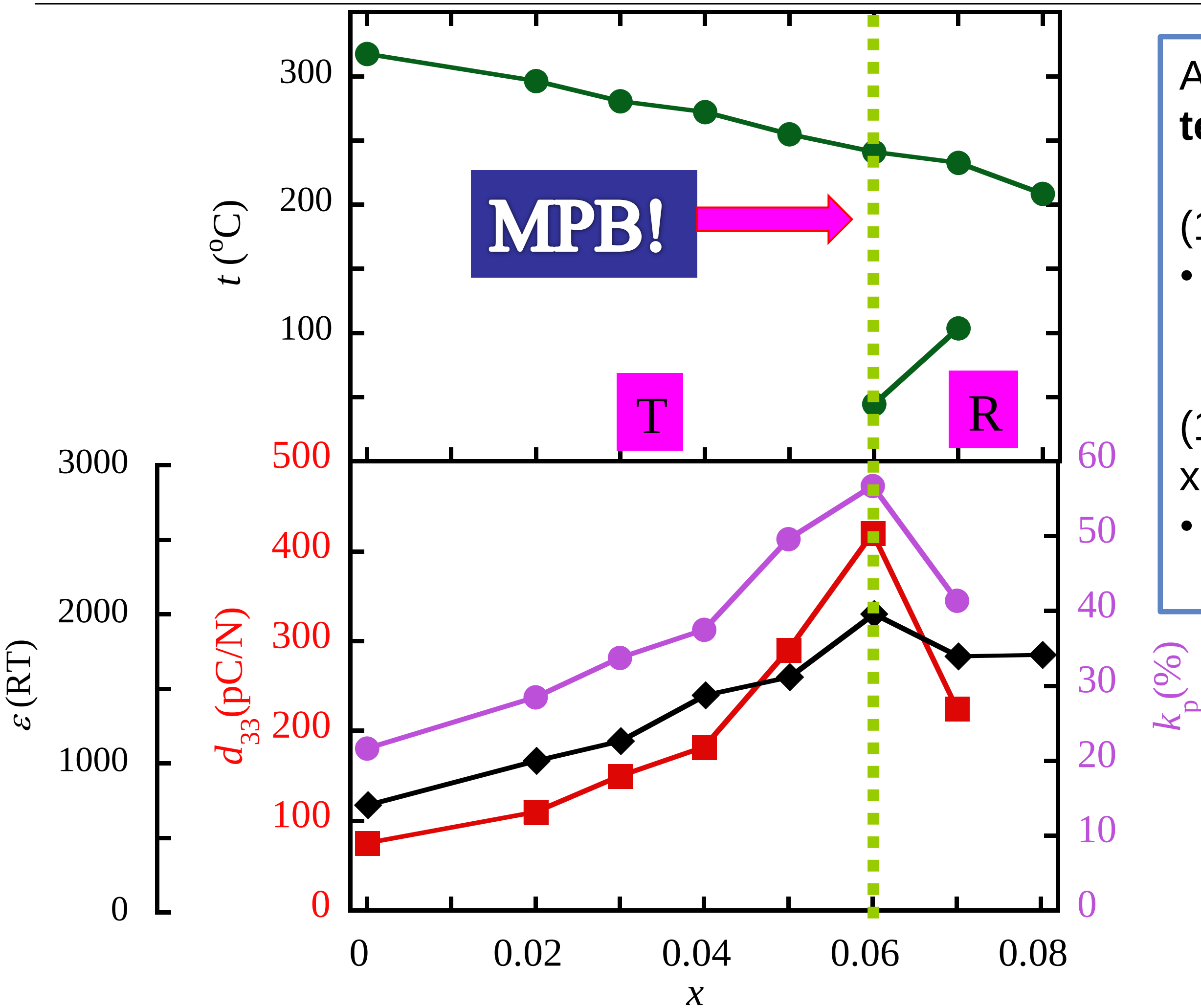


Aim: phase boundary between **tetragonal** and **rhombohedral**

$(1\text{-}x)(Na_{0.5}K_{0.5})NbO_3$–$xBaZrO_3$
- rhombohedral 0.08 ≤ x ≤ 0.15 (RT)

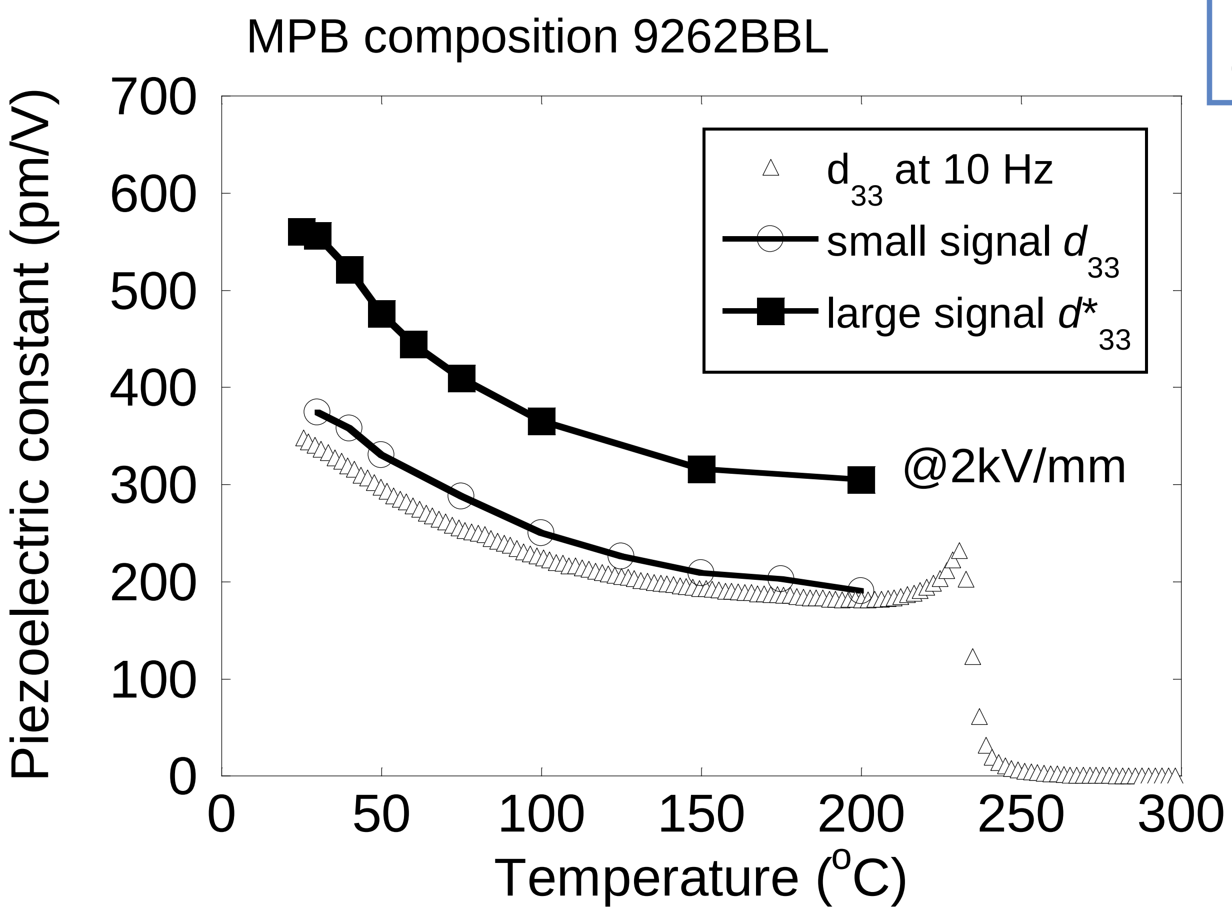
$(1\text{-}x)(Na_{0.5}K_{0.5})NbO_3$–$x(Bi_{0.5}Li_{0.5})TiO_3$
- tetragonal 0.06 ≤ x ≤ 0.15 (RT)

$0.90(Na_{0.5}K_{0.5})NbO_3$–$xBaZrO_3$ –$(0.10\text{-}x)(Bi_{0.5}Li_{0.5})TiO_3$

J. Zushi, R. Wang *et al.*, Jpn .J. Appl. Phys., 52 (2013)

$d_{33}(T)$ in KNN-based MPB material

Ruiping Wang
(AIST, Tsukuba, Japan)



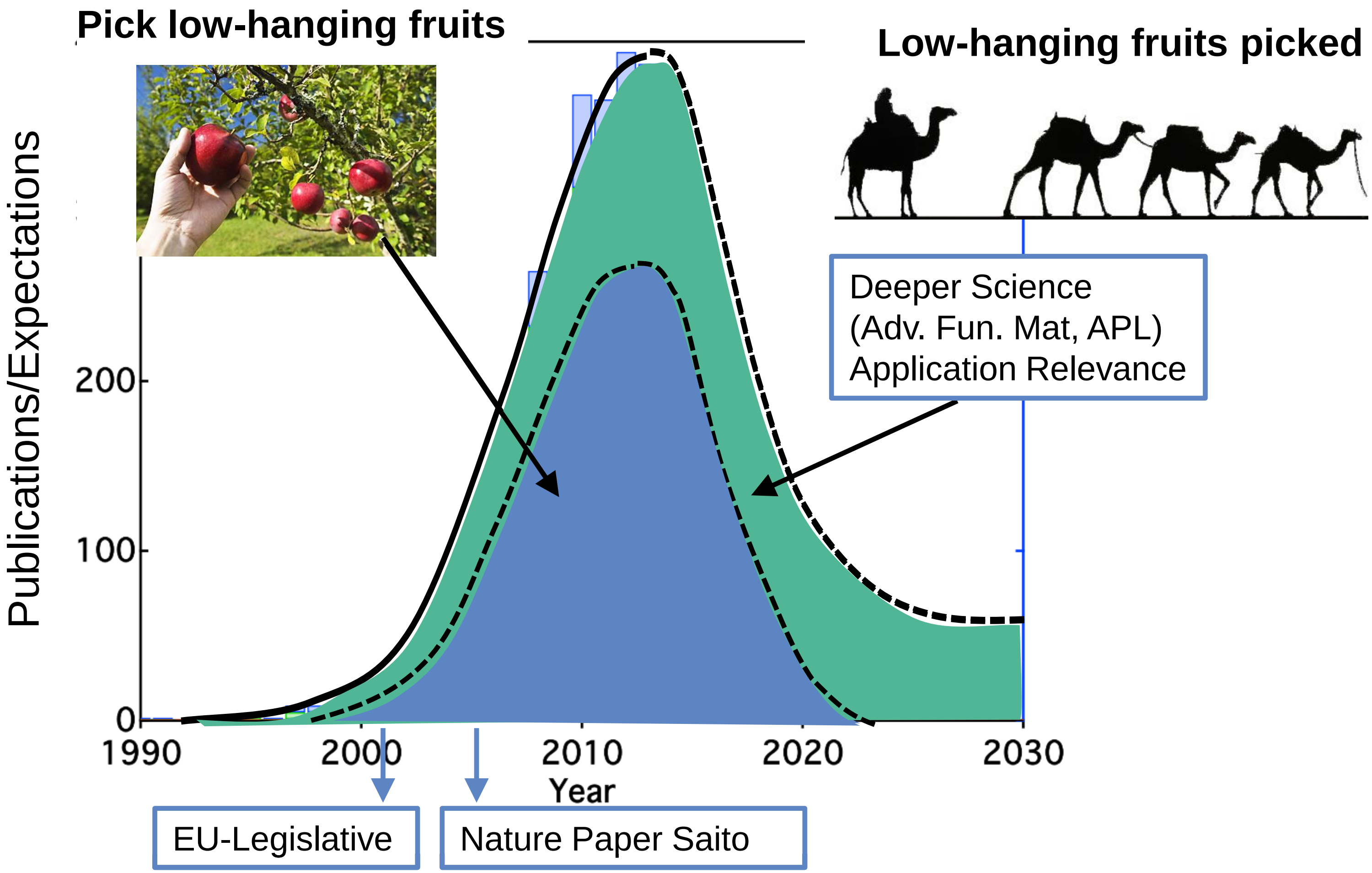
$0.92(Na_{0.5}K_{0.5})NbO_3$-
$x$$BaZrO_3$-
$(0.08-x)(Bi_{0.5}Li_{0.5})TiO_3$

R. Wang *et al., unpublished*

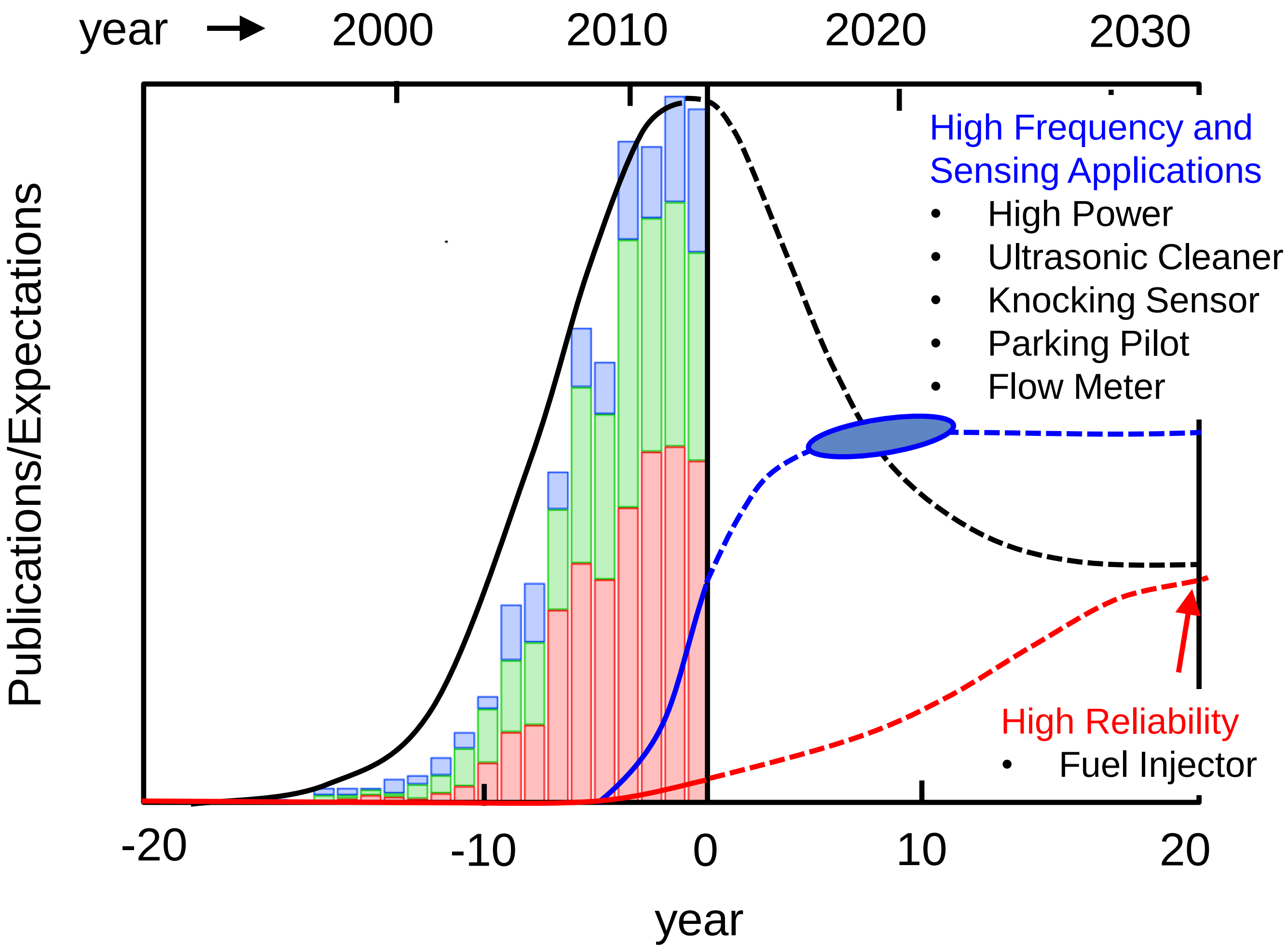
Summary: Innovation management

- Legislation trigger
- Peak of inflated expectations
- Trough of disillusionment
- Transfer enlightenment

Worldwide Research Trend



Industrial Development



Acknowledgements

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TU Darmstadt:

W. Jo, R. Dittmer, S. Schaab, T. Granzow, J. Glaum, E. Anton, E. Sapper, S. Zhang, J. Chen, E. Aulbach, D. Isaia, C. Groh, M. Acosta, J. Zang, H. Zhang, J. Kling, L. Schmitt, M. Hinterstein, A. Kleebe, W. Donner, H. v.Seggern, G. Buntkowsky, P. Braga-Groszewicz, K. Webber. S. Zhukov

Ferroelectrics:

D. Damjanovic (EPF

BNT-based relaxor

A.J. Bell (Leeds Uni (KERI, Korea)

KNN:

K. Wang, J.F. Li (Tsi pan)

BCT-BZT:

M. Ehmke, J. Blendell, (Purdue, USA), K.J. Bowman, (IIT, USA)

Single crystals (BNT-BT):

D. Rytz (FEE, Germany)