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On the electrical conductivity and point defects in $BiFeO_3$-$Bi_{0.5}K_{0.5}TiO_3$ materials

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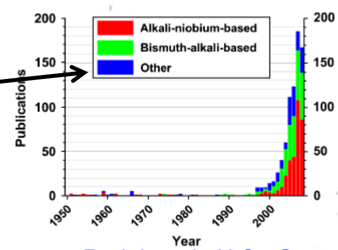
Outline

- BFO-BKT solid solutions
  - Lead-free alternative?
- Lesson learned from
  - Fe-containing perovskites (conductivity)
  - PZT
- Properties of BFO-BKT solid solutions
- Electrical conductivity of 80 and 90 mol% BFO
  - effect of atmosphere
  - Transition from p-type to n-type conductivity
- Mechanical hardening – point defects
- Summary



Rödel et al. JACerS 92 (2009) 1153

Fatigue?

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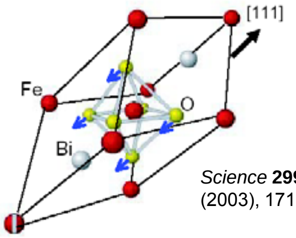
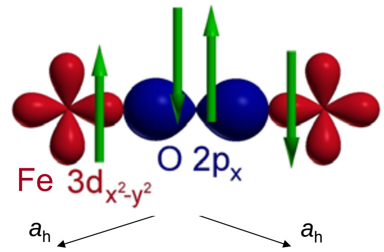
Multiferroic $BiFeO_3$

- Ferroelectricity due to $6s^2$
- $\boldsymbol{P}_S$ || $[111]_{rhomb}$ || $[001]_{hex}$, T_C = 830 °C
- Magnetism: HS d^5 (Fe^{3+})
- Antiferromagnetic due to ~180° coupling through O 2*p*
  T_N = 370 °C



Science **299** (2003), 1719.



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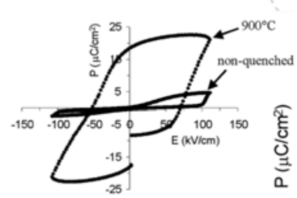
Ferroelectric $BiFeO_3$

- High intrinsic polarization and strain
- Problems: High coercive field, dielectric loss (conductivity), preparation of bulk challenging

- Conductivity: Point defect chemistry
- Hardening and aging:
  - Quenching from above T_C: Coercive field decreased, remnant polarization increased:

    Disordered point defects



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Rojac et al. *JACerS* 97 (2014) 1993

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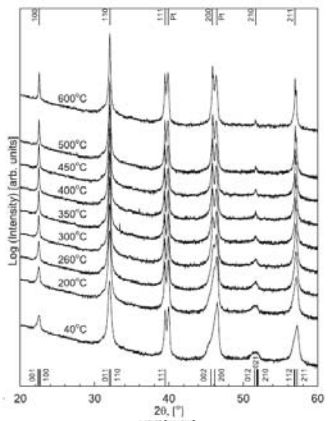
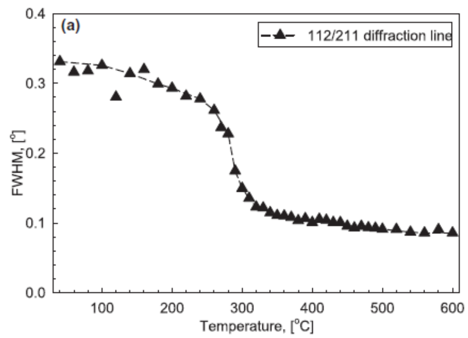
Ferroelectric $Bi_{0.5}K_{0.5}TiO_3$

- Difficult to synthesize?
- Tetragonal, high T_C (380 ºC), relaxor above ~ 300 ºC





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Wefring et al. JACerS 97 (2014) 2928

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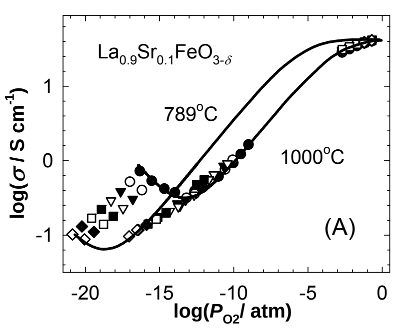
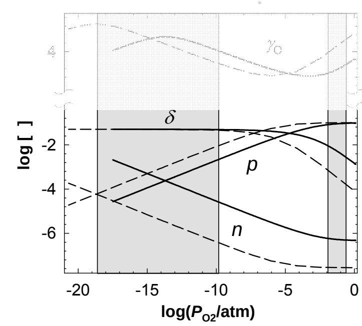
Electrical conductivity of $La_{1-x}Sr_xFeO_{3-\delta}$





- Change from p-type (Fe^{4+}) to n-type (Fe^{2+}) conductivity going from oxidizing to reducing conditions
- $BiFeO_3$ same behavior?
- p_{O2} at the conductivity minimum?

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Wærnhus, Grande, Wiik *Topics Catalysis* 54 (2011) 1009

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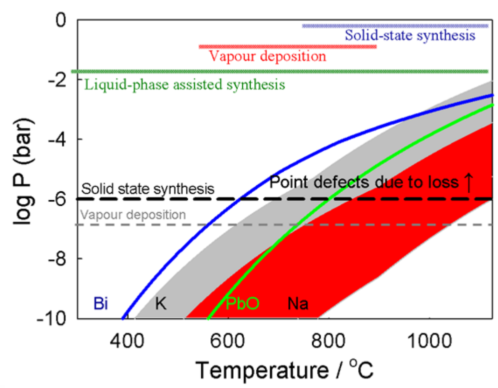
Point defects due to volatile oxides

- A-site elements in ferroelectric oxides volatile
- Volatility challenge for PZT, KNN, BKT, $BiFeO_3$, …..



Estimated vapor pressures

Loss induce point defects

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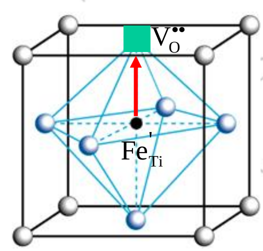
Lesson learned from PZT

$$Pb_{Pb}^{x} + O_{O}^{x} \rightarrow V_{Pb}'' + V_{O}^{\bullet\bullet} + PbO(g)$$

- Loss of PbO compensated for by doping
- Elimination of oxygen vacancies by donor doping (La, Nb), softening
- Introduction of oxygen vacancies by acceptor doping (Fe, Cu), hardening

- Oxygen vacancy diffusion orient “defect dipoles” with respect to polarization direction

- Point defects in BFO-BKT?



$Fe_{Ti}' - V_{O}^{\bullet\bullet}$

Morozov and Damjanovic *J.Appl.Phys.* 107 (2010) 034106
Genenko, Glaum, Hoffmann, Albe, SFB595

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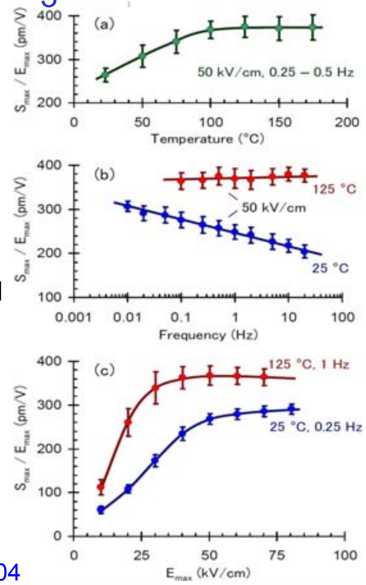
Stable $BiFeO_3$-$Bi_{0.5}K_{0.5}TiO_3$ solid solutions

- Single phase ceramics prepared by conventional solid state synthesis
  - Parasitic phases (as for BFO) not present
  - Rhombohedral BFO-type (100-65% BFO)
  - Tetragonal BKT-type (0-15% BFO)
  - Pseudo-cubic in between
- Maximum dielectric permittivity and field induced strain at 25-30 mol% BFO
- Enhanced performance with increasing temperature for 25 mol% BFO



Morozov, Einarsrud, Grande *APL* 101 (2012) 1252904

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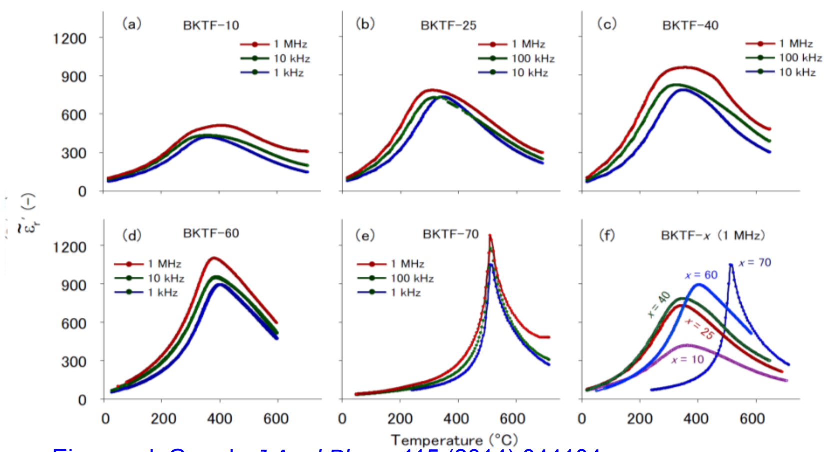
$BiFeO_3$-$Bi_{0.5}K_{0.5}TiO_3$ solid solutions

- MW relaxation below 300 ºC, removed by annealing
- Relaxor-type behavior > 30 mol% BKT



Morozov, Einarsrud, Grande *J.Appl.Phys.* 115 (2014) 044104

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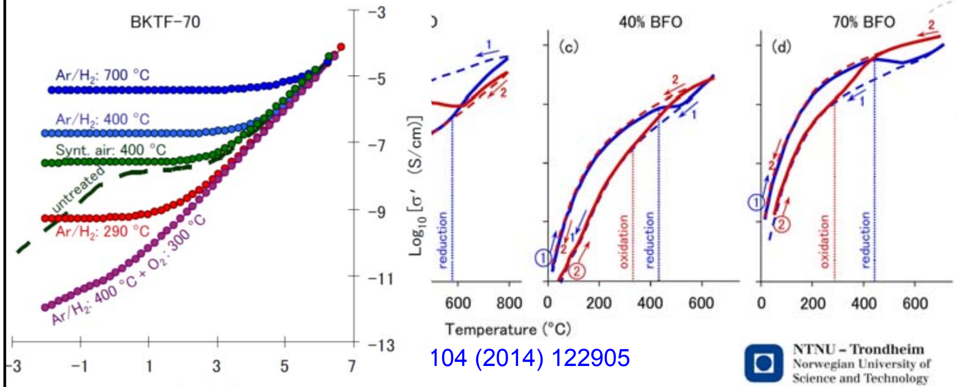
$BiFeO_3$-$Bi_{0.5}K_{0.5}TiO_3$ solid solutions

- Conductivity dependent on partial pressure of oxygen
- Conductivity can be reduced by thermal annealing in reducing atmosphere



104 (2014) 122905

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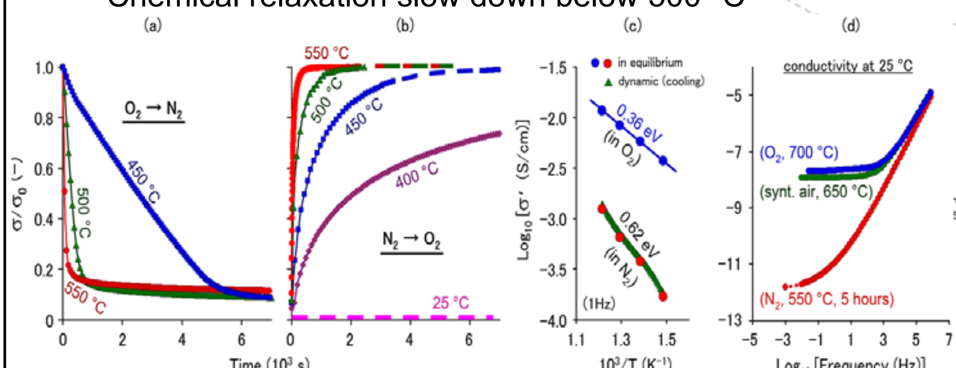
Morozov, Einarsrud, Grande *J.Appl.Phys.* 115 (2014) 044104

$BiFeO_3$-$Bi_{0.5}K_{0.5}TiO_3$ solid solutions

- Open up of strain - electric field hysteresis loops by thermal annealing in inert atmosphere
- Chemical relaxation slow down below 500 ºC



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Morozov, Einarsrud, Grande *APL* 104 (2014) 122905

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$BiFeO_3$-$Bi_{0.5}K_{0.5}TiO_3$ solid solutions

- Electrical conductivity can be controlled by annealing in inert or reducing atmosphere
- Reduced dielectric loss and electrical breakdown – one important step towards utilization of these materials
- Electrical conductivity of BFO-based materials?
- Hardening mechanism(s)?

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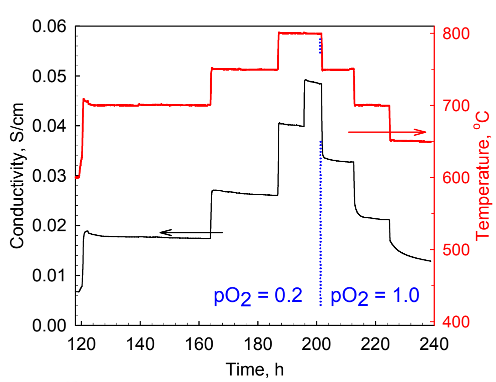
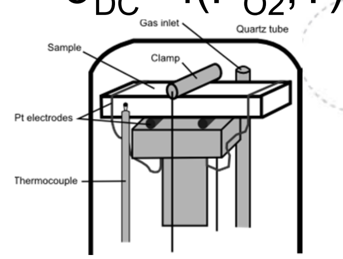
DC conductivity BFO-BKT

- Four point conductivity measurement
- Fix pO_2, vary T, Fix T vary pO_2

$\sigma_{DC} = f(P_{O2}, T)$





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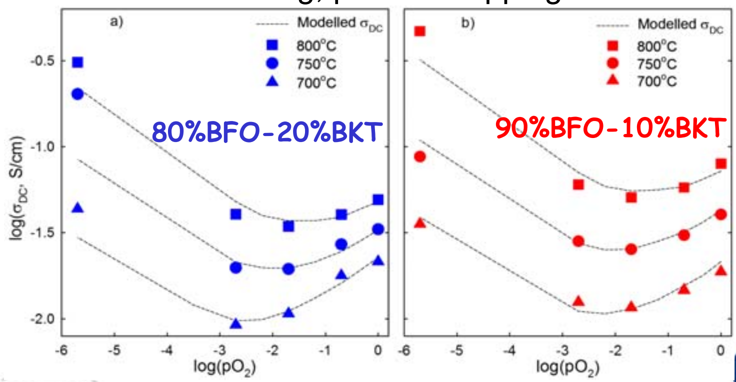
DC conductivity BFO-BKT

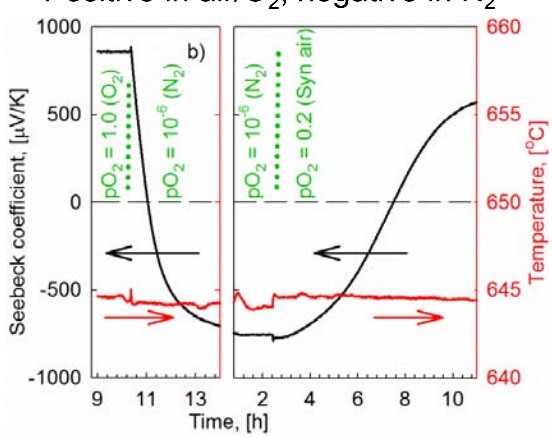
- Minimum in DC conductivity between 10^{-3}-10^{-2} bar O_2
- Change in slope versus pO_2 – from p-type to n-type?
- Semiconducting, polaron hopping

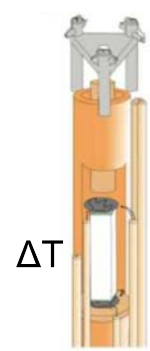


Wefring, Einarsrud, Grande *in preparation*

Seebeck coefficient BFO-BKT

- Positive in air/O_2, negative in N_2





80%BFO-20%BKT

Wefring, Einarsrud, Grande *in preparation*

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Point defect model for σ_{DC}

- Mass action law equilibrium model

$$\sigma_{tot} = \sigma_{ion} + \sigma_e + \sigma_h \approx N_v n e \mu_e + N_v p e \mu_h$$

- Red-ox equilibria involving Fe^{2+}(n), Fe^{3+}, Fe^{4+}(p)

$$V_O^{\bullet\bullet} + 2Fe_{Fe}^{\times} + \tfrac{1}{2}O_2(g) \rightleftharpoons 2Fe_{Fe}^{\bullet} + O_O^{\times}$$

$$V_O^{\bullet\bullet} + 2Fe_{Fe}^{'} + \tfrac{1}{2}O_2(g) \rightleftharpoons 2Fe_{Fe}^{\times} + O_O^{\times}$$

- Loss of A-site ions, mass balance Fe and electron neutrality

$$aA_A^{\times} + oO_O^{\times} \rightarrow aV_A^{(3-x)'} + oV_O^{\bullet\bullet} + aA(g) + \tfrac{o}{a}O_2(g)$$

$$(1 - x_{BKT}) = n + \left[Fe_{Fe}^{\times}\right] + p$$

$$p + 2\left[V_O^{\bullet\bullet}\right] = n + (3 - x_{BKT})\left[V_A^{(3-x)'}\right]$$

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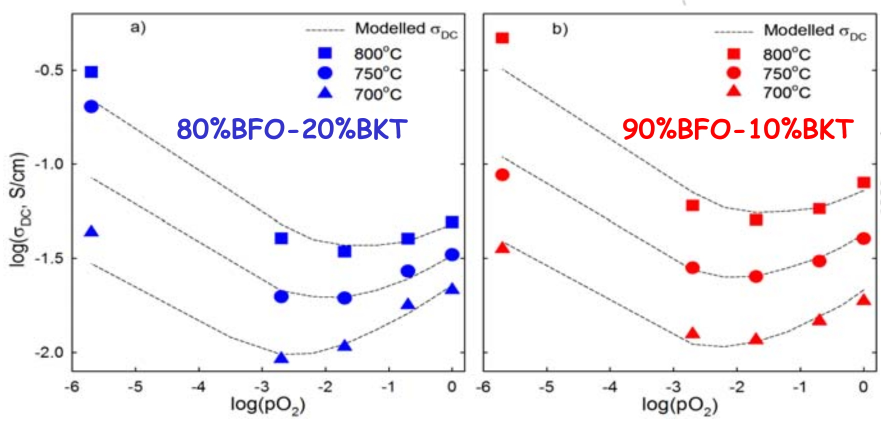
DC conductivity BFO-BKT



- P-type in air or oxygen
- N-type in inert atmosphere

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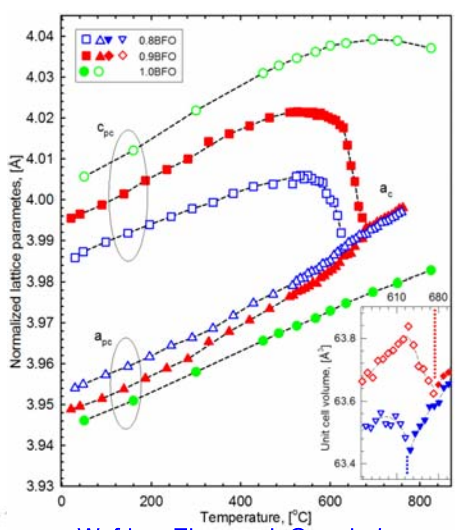
Conductivity of BFO-BKT

- Semiconductor, polaron hopping
- p-type in air/oxygen, n-type in inert/reducing atm

- Conductivity can be minimized by annealing in inert or reducing atm

- Electrical conductivity – p-type to n-type
  - screening of polarization field
  - charge domain walls

Currie temp. BFO-BKT (BFO-type)



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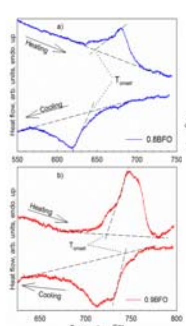
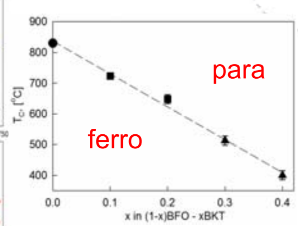
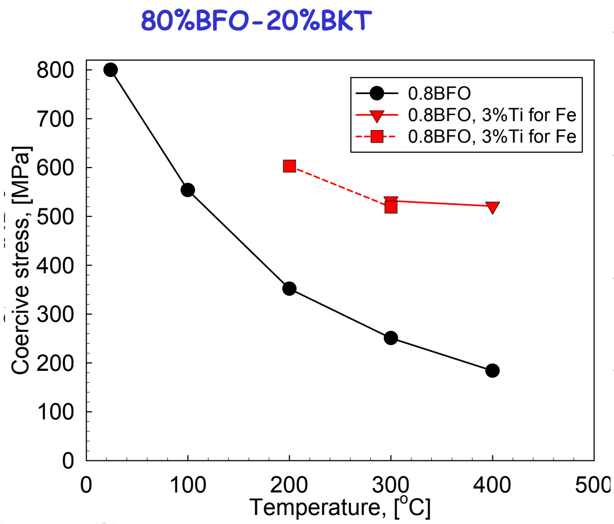
- T_C remains relatively high up to 30-40 % BKT
- High strain reduced with BKT
- I. order phase transition





Mechanical hardening of BFO-BKT



- Compressional Stress-strain measurement
- Opening of hysteresis loop by quenching
- High coercive field
- Hardening mechanism?

Wefring, Webber et al., *in preparation*

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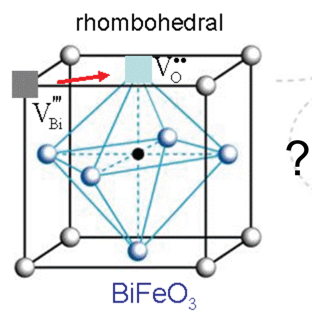
Possible hardening mechanism(s)

- High T_C; Point defects mobile in ferroelectric state
- Mechanical softening by quenching from above T_C
  - Defect dipoles?



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Summary

- BFO-BKT solid solutions stable; three phases, tetragonal (BKT), pseudocubic (relaxor), rhombohedral (BFO)
  - Maximum dielectric constant and electrical field induced strain 25% BFO
  - Temperature stable performance up to at least 170 ºC
  - Reduced dielectric loss/break down by annealing in inert atmosphere; Opening of strain-electrical hysteresis loop BFO-based materials
- Electrical conductivity of BFO-materials
  - Semiconducting, polaron hopping (localized electrons)
  - Change from p-tope to n-type conductivity by pO_2
  - Minimum in conductivity - reduce dielectric loss by annealing in inert atm
- Electrical conductivity minimized by post sintering annealing – opening of hysteresis loop

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Acknowledgement

- Espen Wefring, Maxim Morozov, Mari-Ann Einarsrud Trondheim
- Kyle Webber, Darmstadt
- Sverre M. Selbach, Trondheim

- Research Council of Norway, NTNU

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