Low Temperature Sintering of PZT

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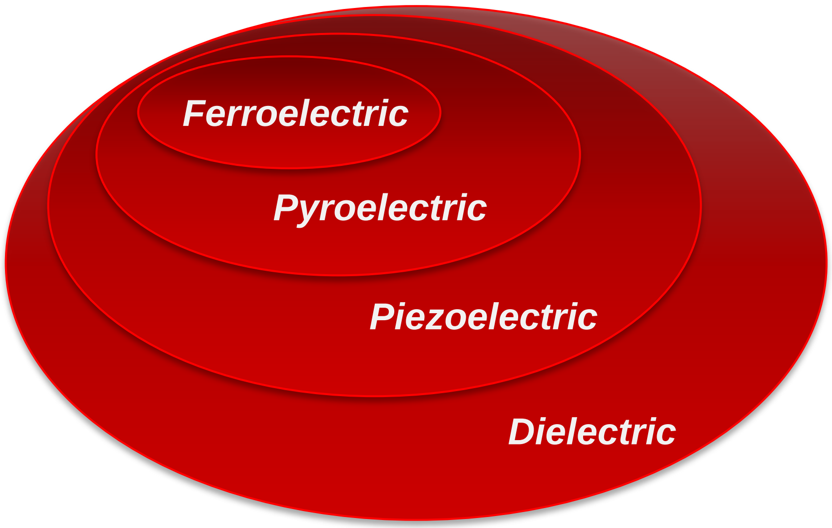
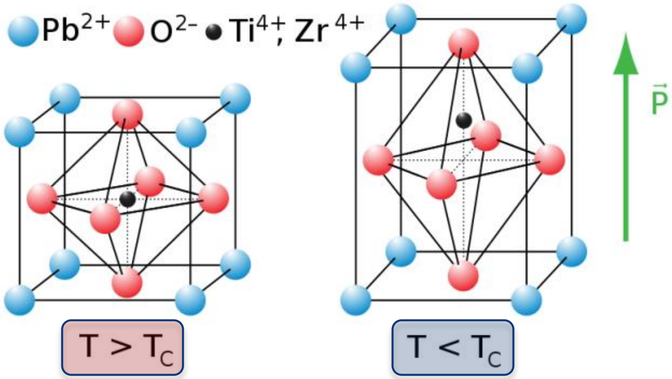
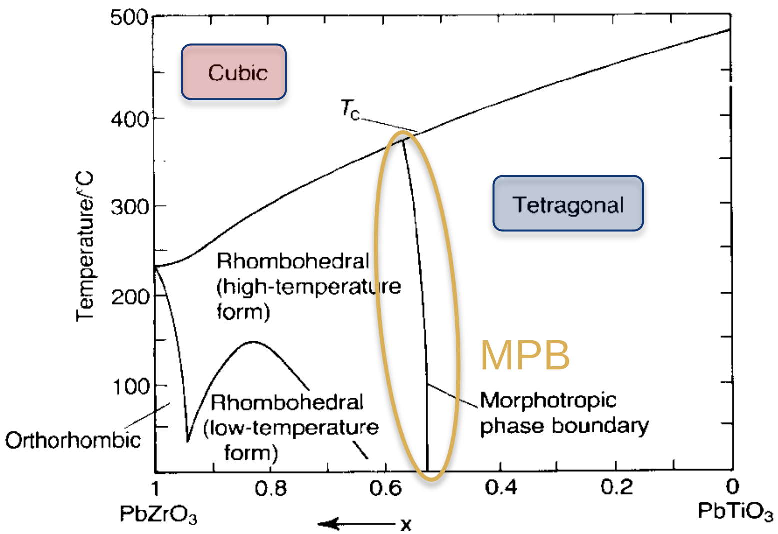
PZT

$Pb(Zr_xTi_{1-x})O_3$

- Solid solution of $PbZrO_3$ and $PbTiO_3$
- Ferroelectric functional ceramic
- Properties sensitive to Zr/Ti ratio
- Largest electromechanical coupling factor at the MPB: Zr / Ti = 52 / 48







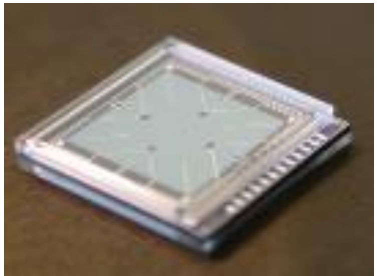
Phase diagram PZT
(Moulson/ Herbert, Electroceramics)

Application using PZT films

Actuators
- Micromotors
- Micropumps

PICMA Stack Actuator
(PI Ceramic GmbH)

Sensors
- Displacement sensors
- Proximity sensors
- Pressure sensors
- Force sensors

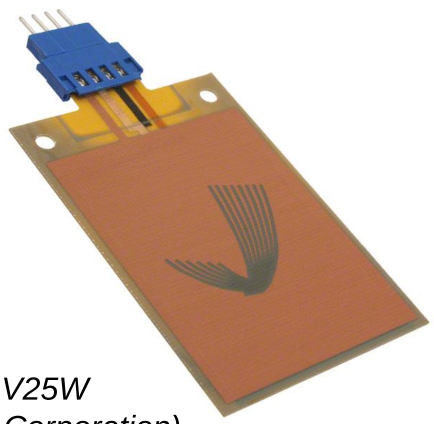


Pressure Sensor
(SINTEF, Norway)

Capacitors
- Ferroelectric RAMs

FeRAM Device
(Fujitsu Semiconductor Europe)

Transducers
- Lamb wave pumps
- **Energy harvesters**

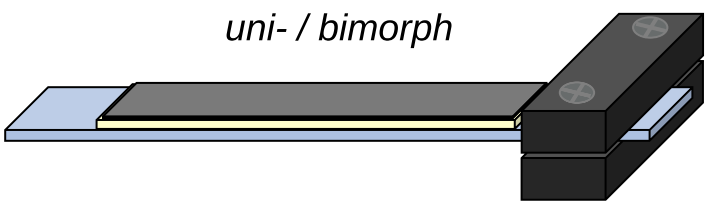


Energy Harvester V25W
(Mide Technology Corporation)

Fabrication of PZT films

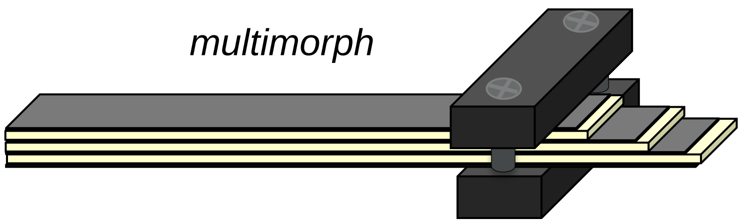
Thin films < 3µm

- Deposition on glass/silicon/metal substrates
- CSD, CVD, PLD, Sputtering, EPD



Thick films > 50 µm

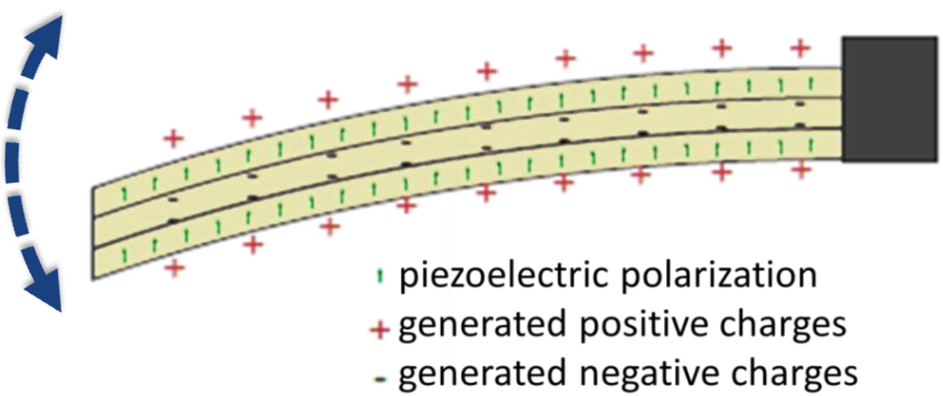
- No need for a substrate
- Tape casting methode



MULTILAYER

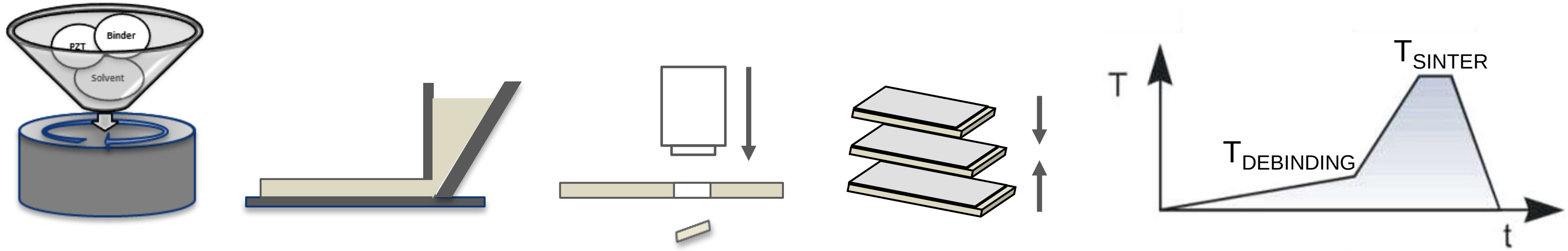
PIEZOELECTRIC

BENDING TRANSDUCER

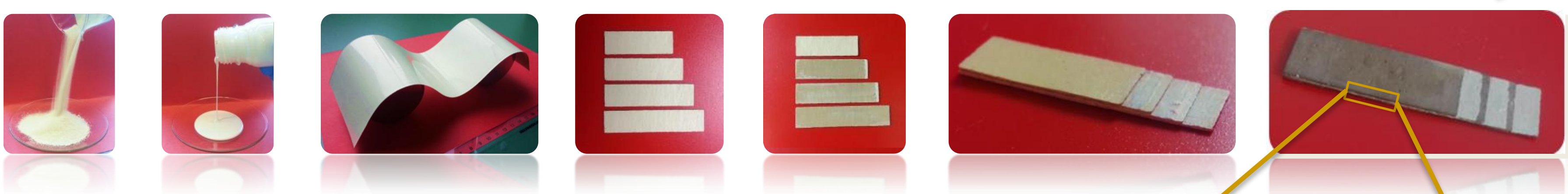


C. Eichhorn, 2011

Ceramic Multilayer Technology

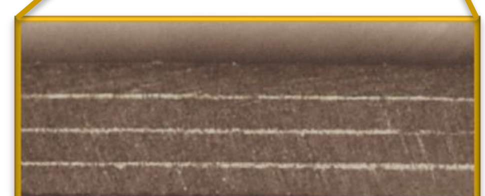


Powder | Slurry | Green Tape | Single Layers | Metallized Layers | Green Multilayer Stack | Co-fired Multilayer Stack

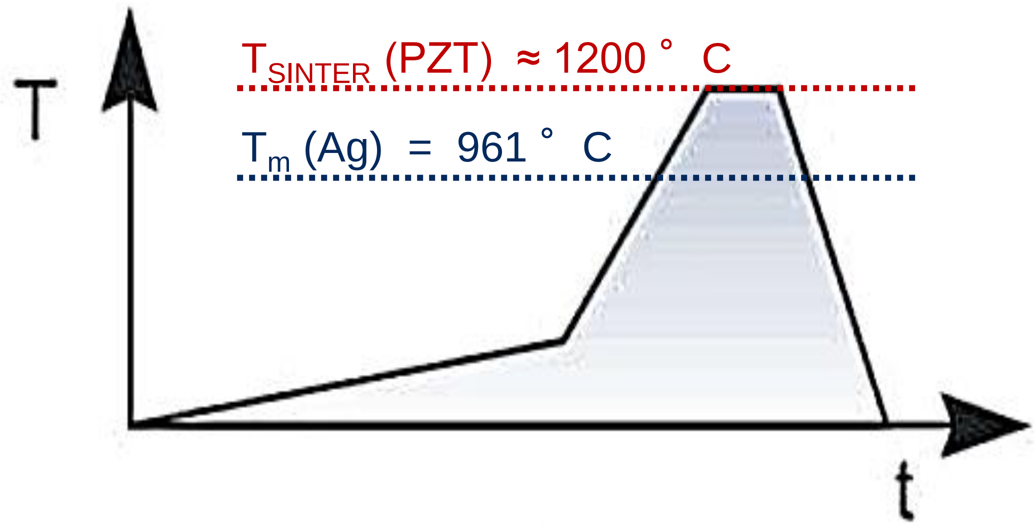


NEW:

Piezoelectric Multilayer
with
Ag-Electrodes



Challenge: Material Compatibility



PZT-ML are fabricated with high temperature stable inner electrodes from Pt or Ag/Pd alloys

Ag can not be co-fired together with PZT

⇩

Low Temperature Co-fired Piezo Ceramic

Metall prices [US-$/oz]

Ag	**14.77**
Pd	703.87
Pt	1,100.81

Source: finanzen.net, 18.11.2014

Further Benefits of PZT-based LTCC

MATERIAL COMPATIBILITY	STABILIZATION OF ELECTROMECH. PROP.	REDUCTION OF PROCESS COSTS
Co-firing of Hybrid ML structures with **integrated LTCC-Layers**	**Reduction of evaporation of volatile PbO** out of PZT during the sintering process, so that the subsequent piezoelectric **components** become **more reliable**	**Less environmental pollution** through less evaporation of Pb-compounds **Less energy consumption** through lowered sintering temperatures

Approaches for Lowering the T_{SINTER}

1 | Hot-pressing in oxygen

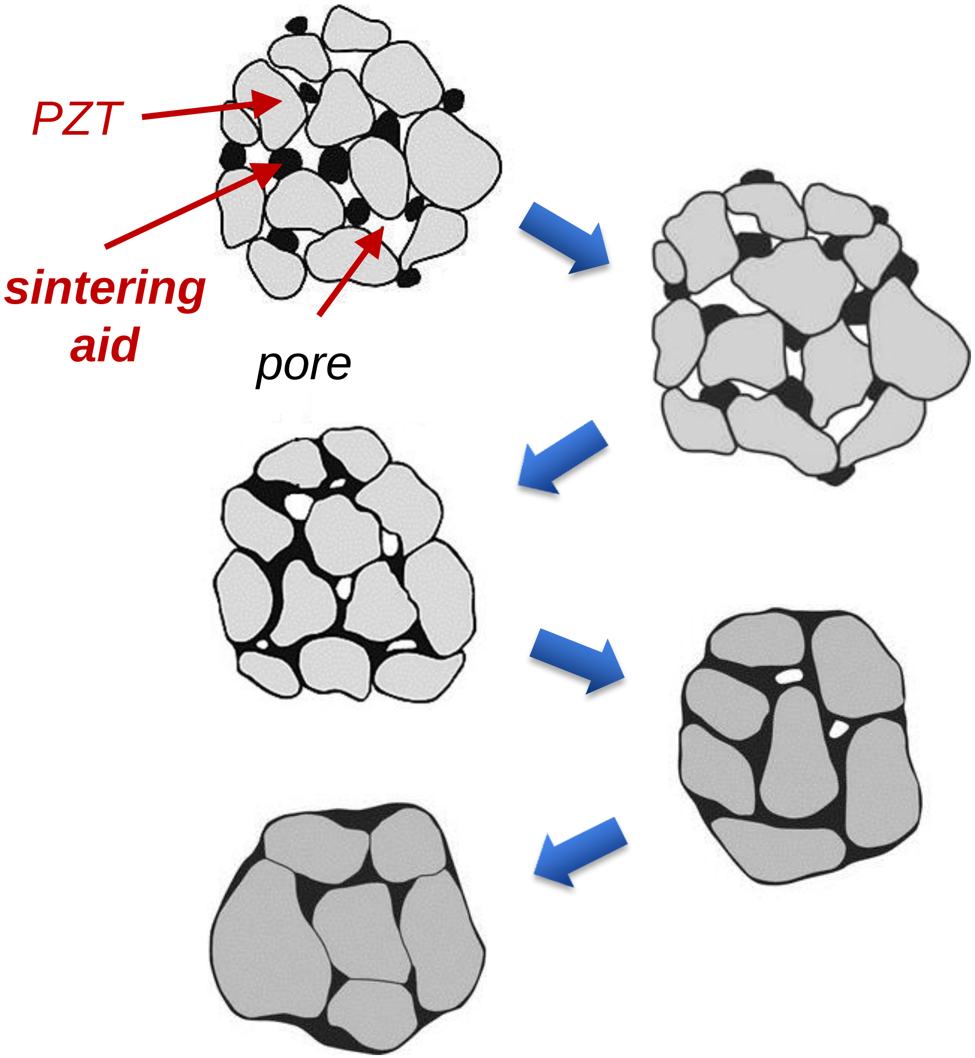
2 | Vacuumed-air-venting process

3 | Using fine ball-milled powders

4 | Using bimodal powders

5 | **Liquid Phase Sintering Technology**

Liquid Phase Sintering Technology



1. **Incorporation of low-melting metal oxides** into the ‘green’ unsintered ceramic

2. **Formation of a liquid-phase** at temperatures about 600 to 800 ° C

3. **Acceleration of densification** through facilitating the PZT particles rearrangement

4. **Formation of sintering necks** with subsequent grain growth

Commercial Ferroelectric Hard PZT

PIC 181 (PI Ceramic)

- Withstands high mechanical and electrical stresses
- Properties change only hardly in dynamic long-term operations
- Relatively low permittivity
- High electromechanical coupling factors
- Very low dielectric losses
- Very high mechanical quality factor

T_C	330 °C
$\varepsilon_{33}^T/\varepsilon_0$	1200
$\varepsilon_{11}^T/\varepsilon_0$	1500
$\tan\delta$	$< 3 \cdot 10^{-3}$
k_{31}	0.33
k_{33}	0.66
k_p	0.56
d_{31}	-120 pC/N
d_{33}	265 pC/N
Qm	**2000**

➡ *well suited for vibration energy harvesters driven in continuous use in resonance mode with only low intrinsic warming of the component*

Investigated Sintering Aids

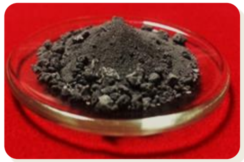
1

2

3

4

5



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Aid:	**Li_2CO_3**	**Li_2O**	**Bi_2O_3**	**V_2O_5**	**MnO_2**	**PbO**
T_m:	720°C	1427°C	817°C	690°C	535°C	888°C
Lit.:	Han et al., 2011, Korea Yoo et al., 2005 Japan	Lee et al., 2005, Korea Jin et al., 2003, Korea	Wang et al., 1992, China	Seo et al., 2011, Korea	Corker et al., 2000, Denmark	Ahn et al., 2006, Korea

7

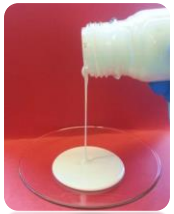
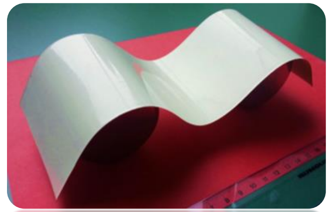
8

9

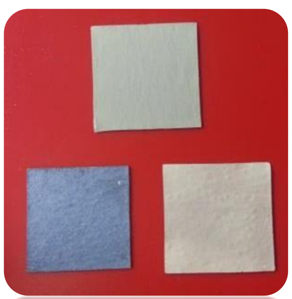
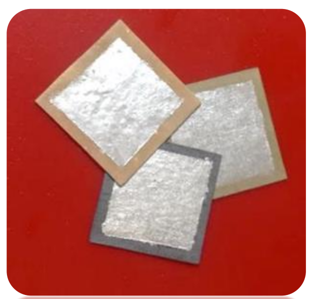
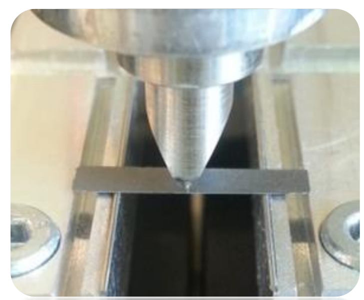
10

Aid:	**$Cu_2O \cdot PbO$ (4:1)**	**$PbO \cdot WO_3$ (5:1)**	**$Li_2CO_3 \cdot Bi_2O_3 \cdot CuO$ (1:1:4)**	**CuO**
T_m:	680°C	730°C	no PD available	1326°C
Lit.:	Corker et al., 2000, Denmark	Vötsch et al., 2007, Austria Nielsen et al., 2002, Slovenia	Yoo et al., 2004, Korea Wang et al., 2000, Japan	Nam et al., 2011, Korea Lee et al., 2000, Korea

Preparation and Characterization of 20 different PZT-Sintering Aid Combinations


… for each SA
in 2 volume fractions:
2 vol.% and 5 vol.%

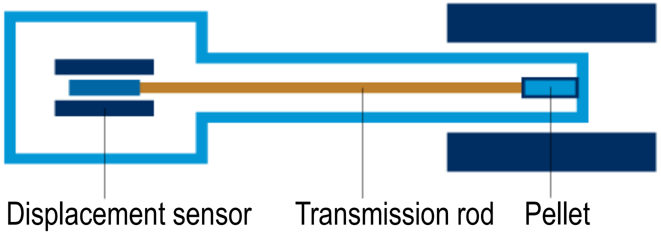
Micro-structure	**Piezoelectric properties**	**Mechanical stability**	**Thermal behavior**
			
porosity density	*charge constant* d_{33}	*breaking strength* σ_0	T_{SINTER}

Thermal Behavior

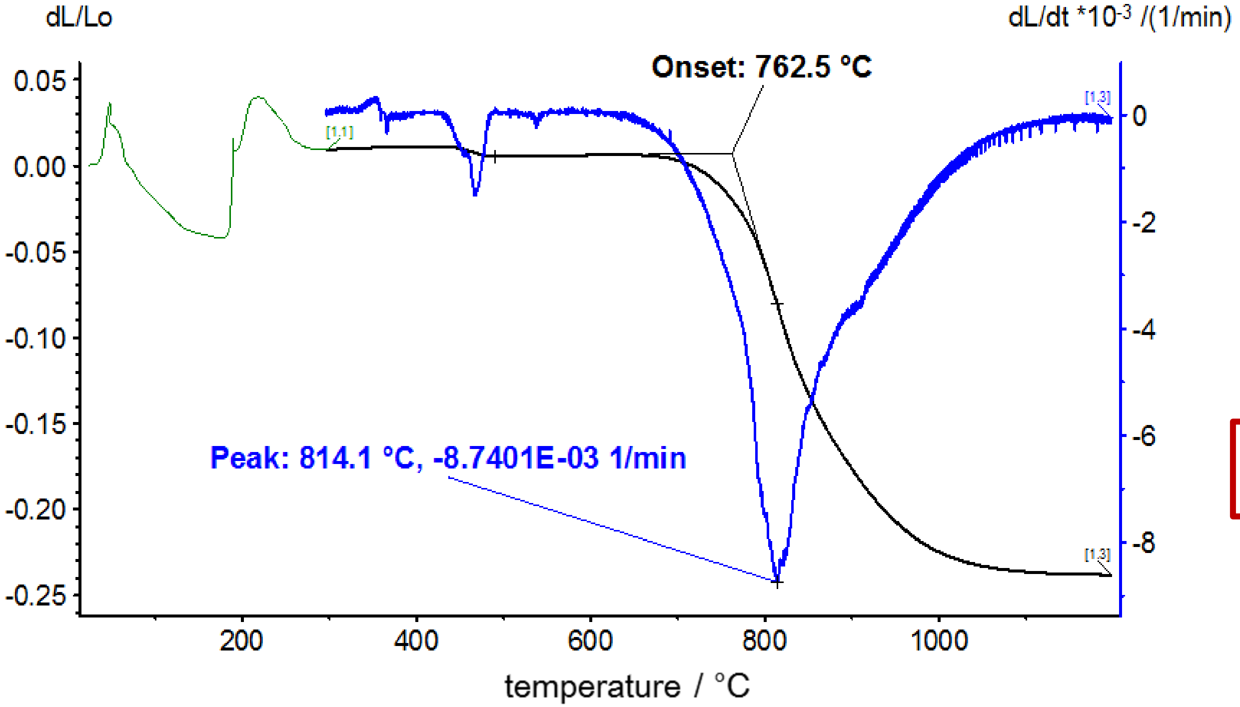
Source: TA Instruments

Dilatometry:

Detection of pellet shrinkage



Length ↓ with T ↑



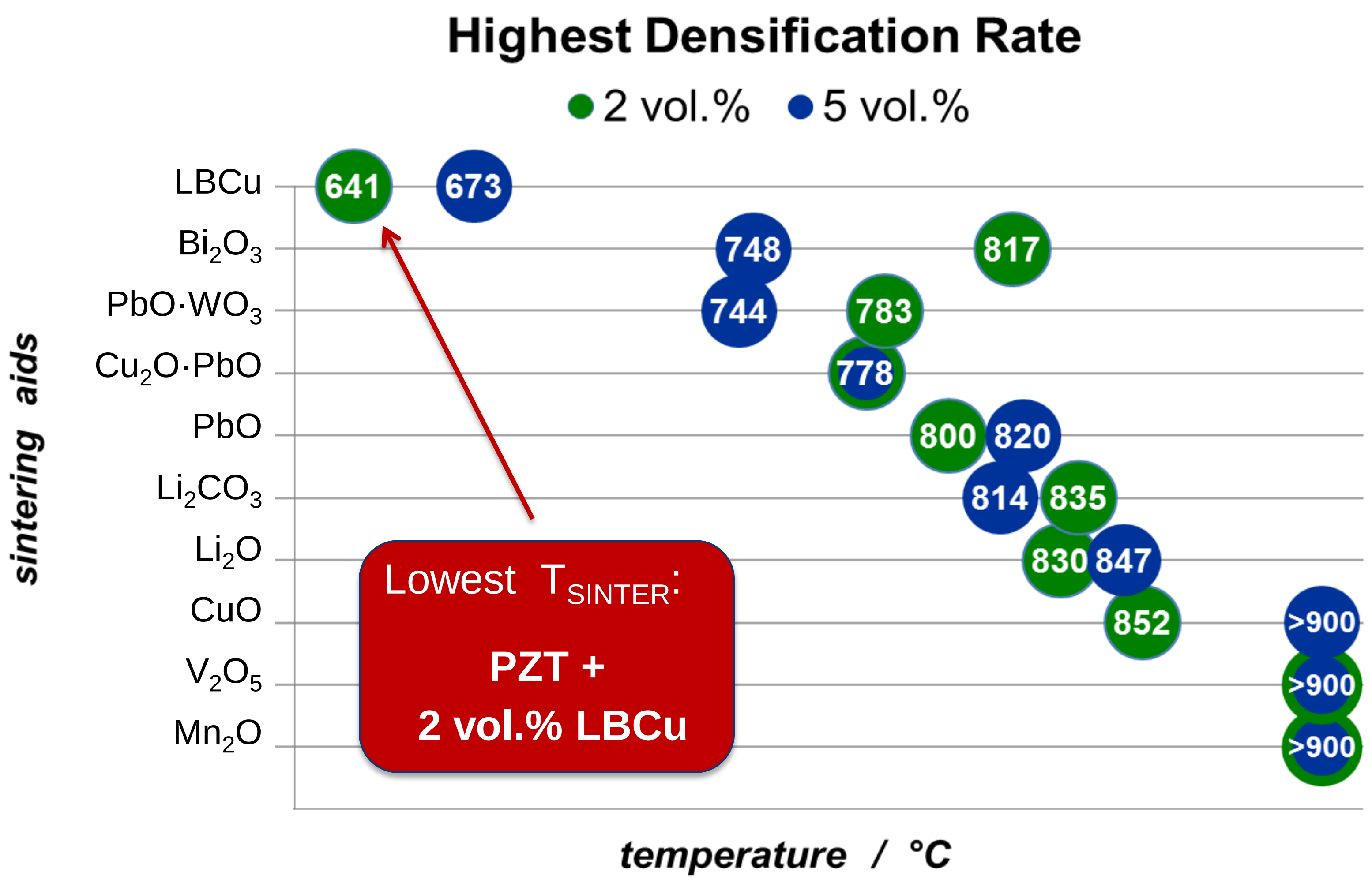
Result for the composition:

PZT +

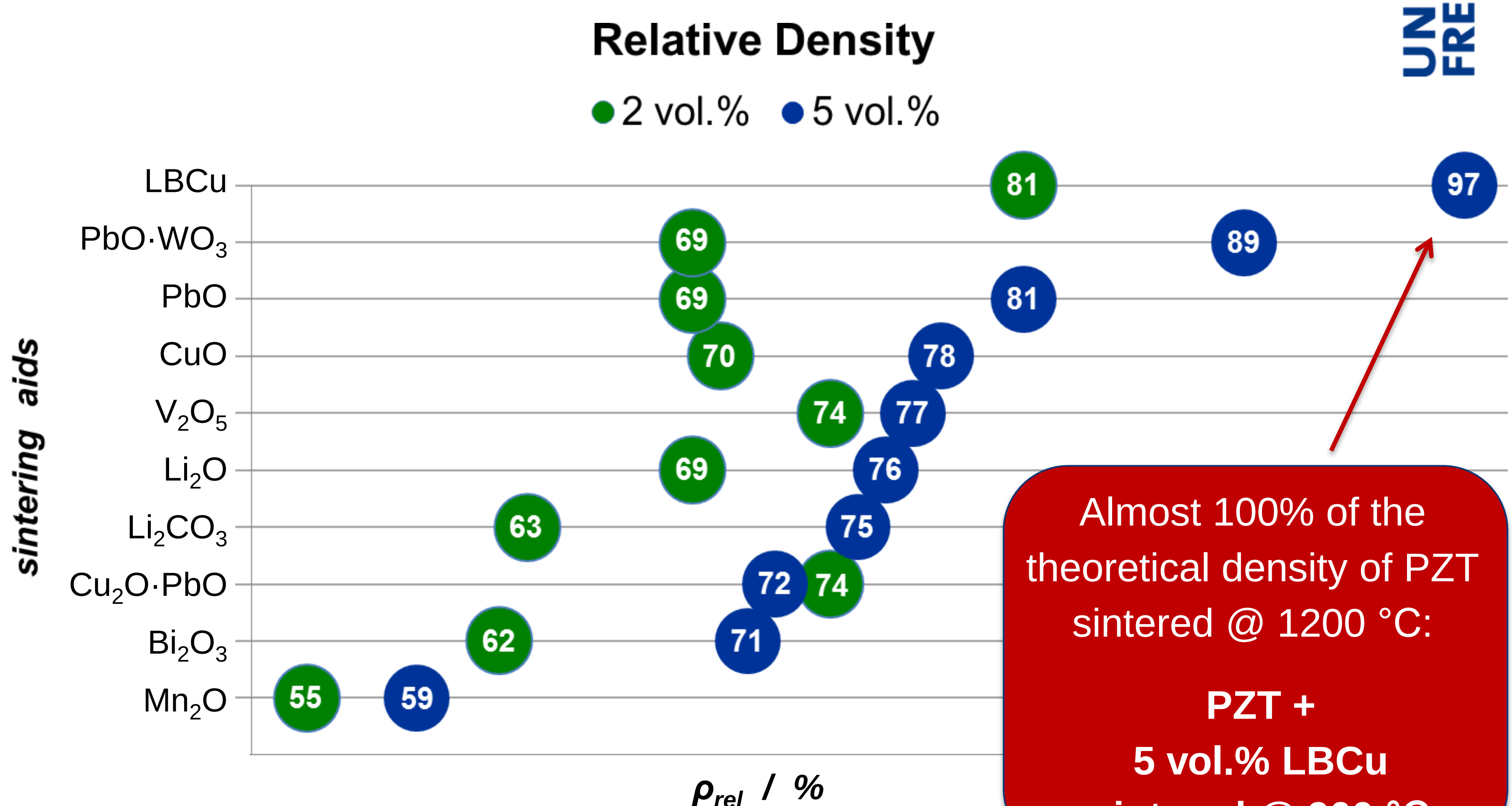
2 vol.% Li_2CO_3

T_{SINTER} = 814 ° C

Thermal Behavior



Microstructure

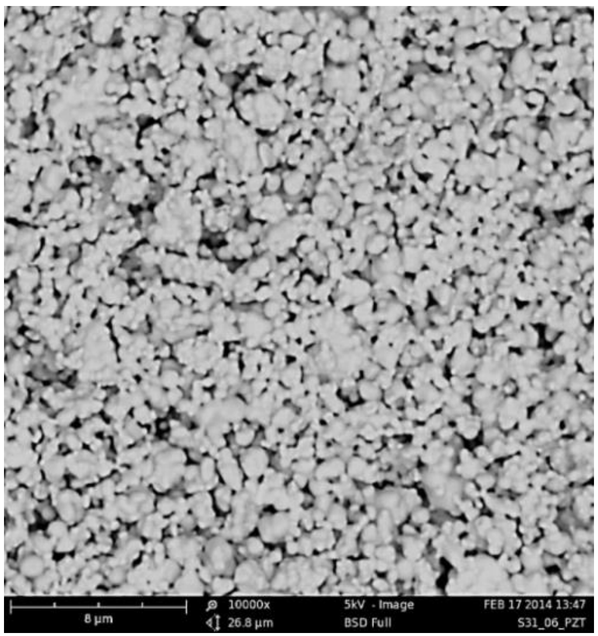


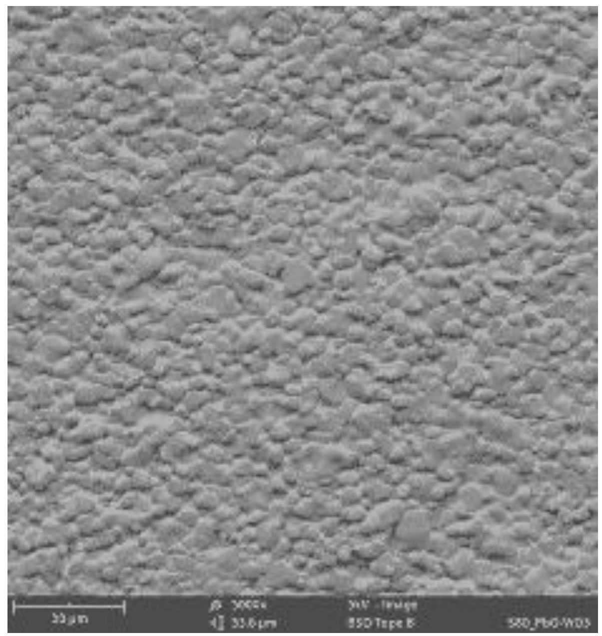
Almost 100% of the theoretical density of PZT sintered @ 1200 °C:

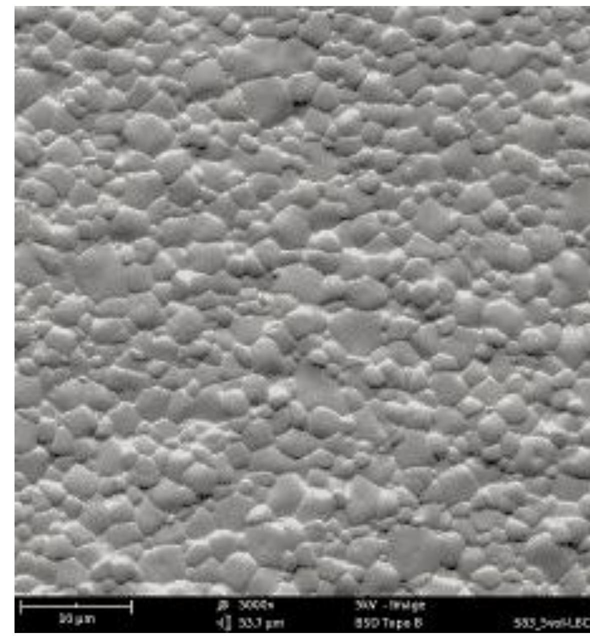
PZT +
5 vol.% LBCu
sintered @ 900 °C

Microstructure

PZT	PZT + 5 vol.% $PbO{\cdot}WO_3$	PZT + 5 vol.% LBCu







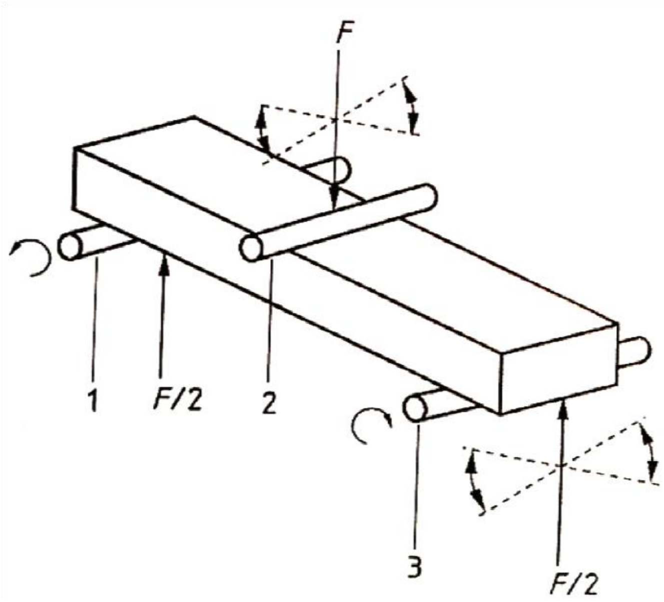
porous

dense @ 900 ° C

Mechanical Stability

<u>Performed</u>:

3-point-bending tests according to DIN EN 843-1 on > 10 specimens for each PZT-SA composition



<u>Measured</u>:

Breaking strength of each specimen

$$\sigma_f = \frac{3 \cdot F \cdot d}{2 \cdot b \cdot h^2}$$

<u>Evaluated</u>:

Characteristic breaking strengths

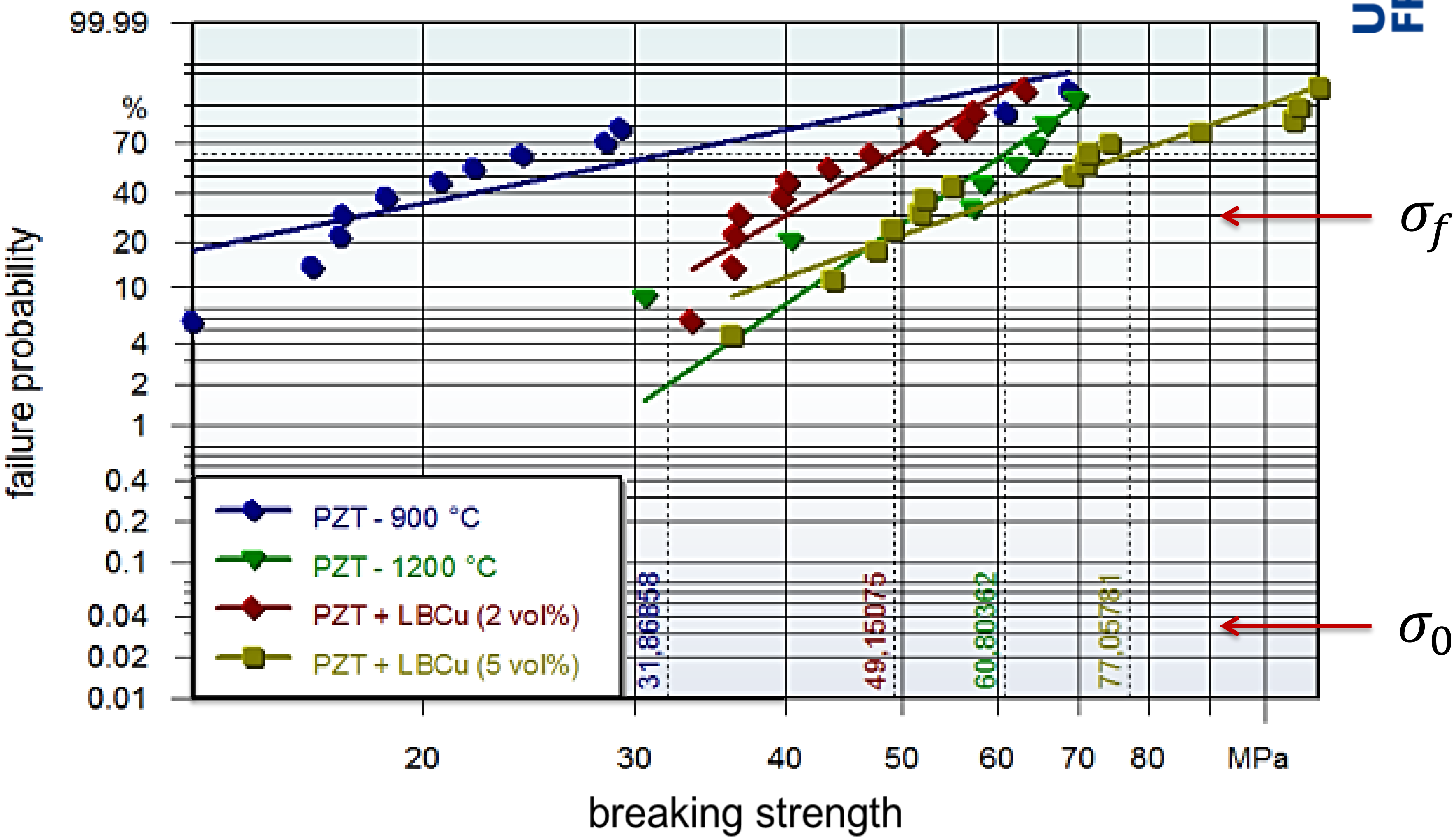
with Weibull statistic

$$\boxed{P_V\left(\sigma_f\right) = 1 - \exp\left(-\left(\frac{\sigma_f}{\sigma_0}\right)^m\right)}$$

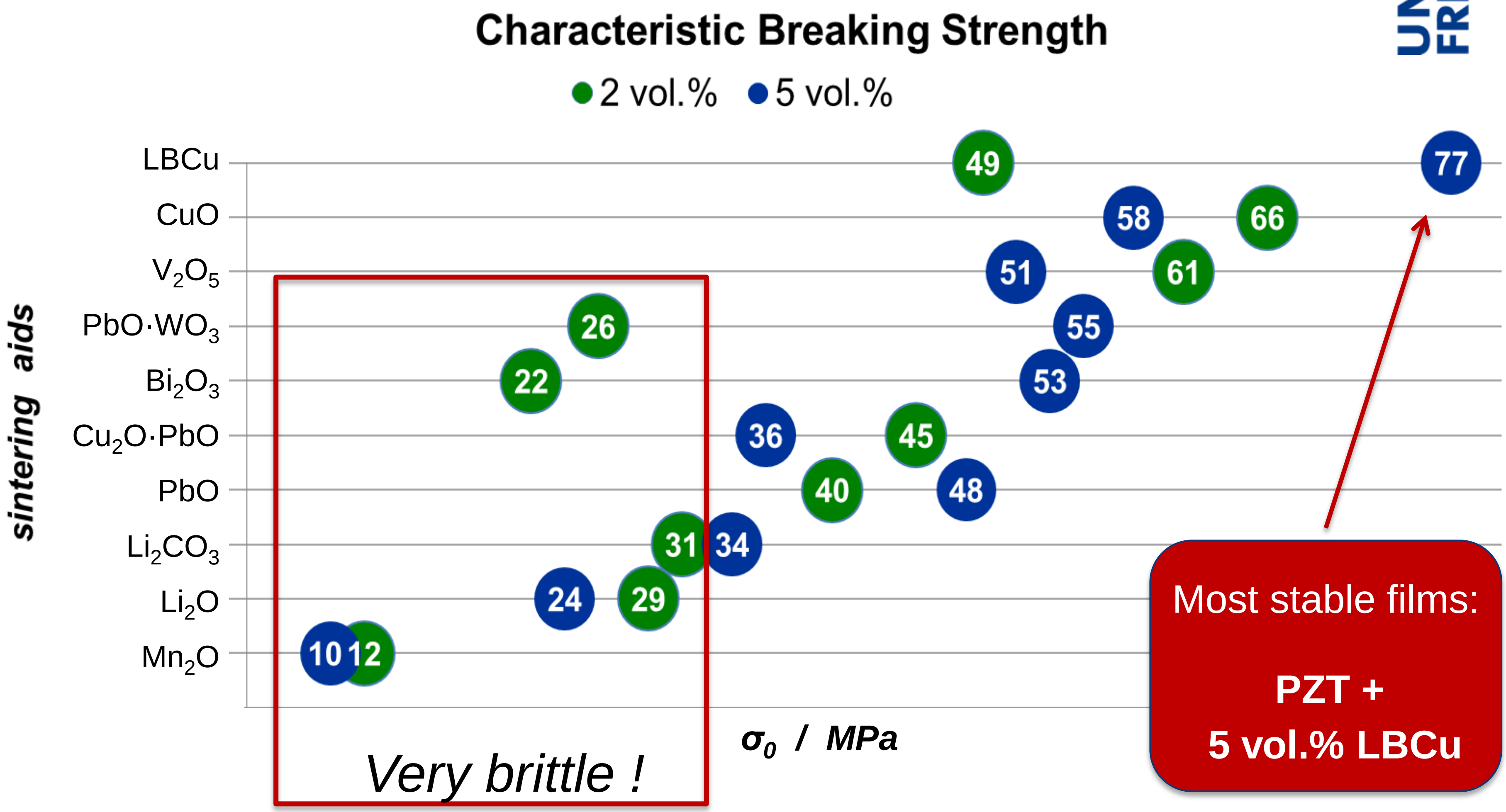
using Maximum-Likelihood-Methode

$$\boxed{L = \prod_{j=1}^{N}\left(\frac{m}{\sigma_0}\right)\left(\frac{\sigma_{fj}}{\sigma_0}\right)^{m-1} \exp\left[-\left(\frac{\sigma_{fj}}{\sigma_0}\right)^m\right]}$$

Mechanical Stability



Mechanical Stability

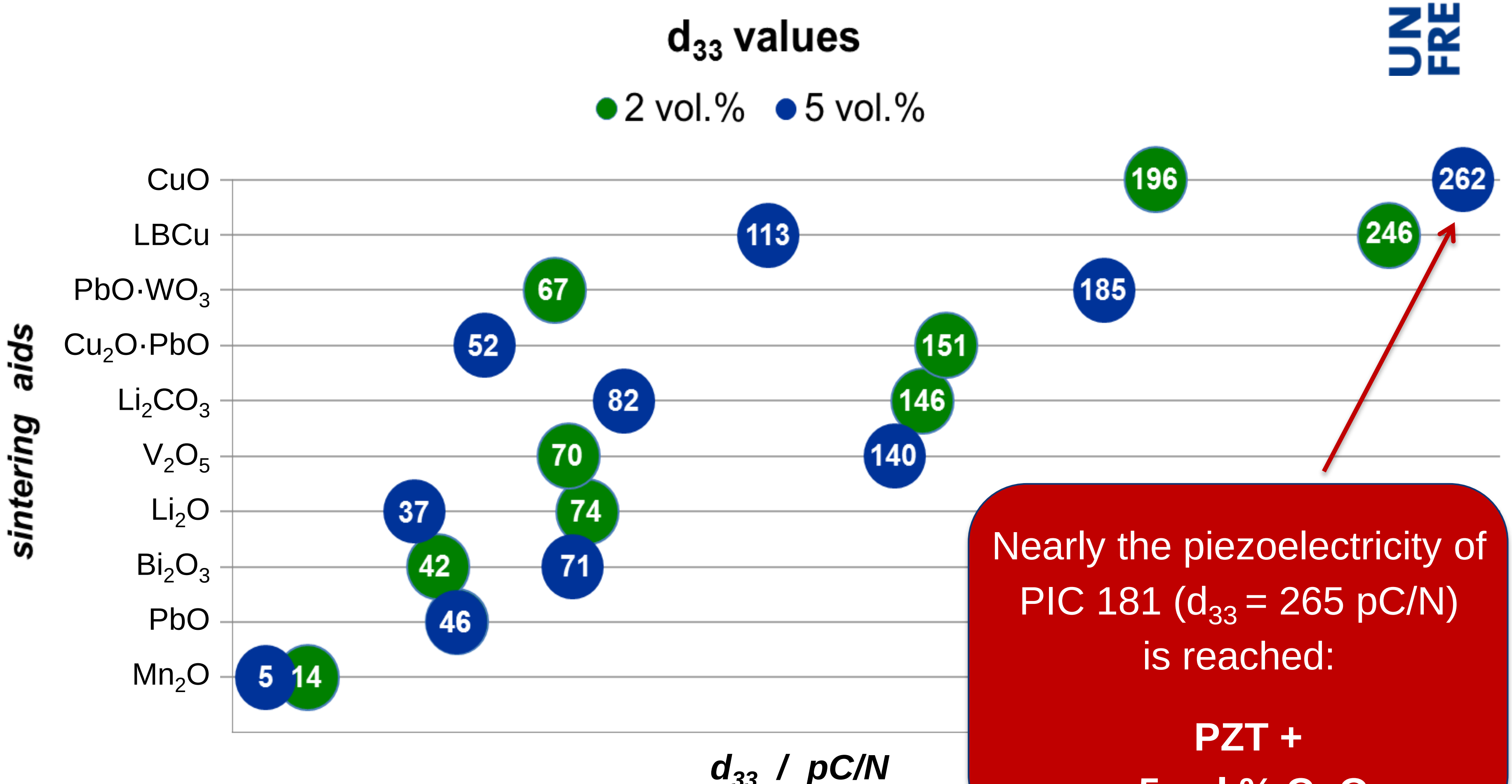


Most stable films:

PZT +

5 vol.% LBCu

Piezoelectric Properties



Nearly the piezoelectricity of PIC 181 (d_{33} = 265 pC/N) is reached:

PZT + 5 vol.% CuO

Conclusion

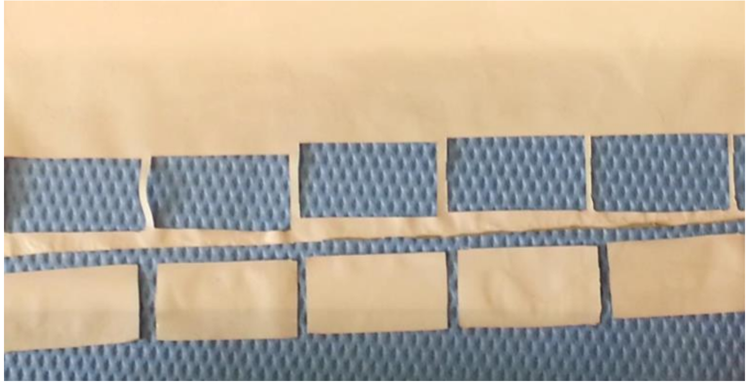
- We fabricated piezoelectric **ML with inner electrodes from pure Ag**
- **10 sintering aids for hard PZT** have been investigated
- **Mechanical stability I microstructure I thermal behavior I piezoel. prop.** of low temperature sintered thick films (t ≈ 100 µm) were studied
- **Films made of PZT + LBCu sintered @ 900 ° C** shows
  a) Lowest T_{SINTER} (641°C)
  b) Highest density (ρ_{rel} = 97%)
  c) Highest mechanical stability (σ_0 = 77 MPa)
  d) High piezoelectric properties (d_{33} = 246 pC/N)
- Addition **CuO** has a **positive effect on the piezoelectric properties** of PZT

Thank You

for

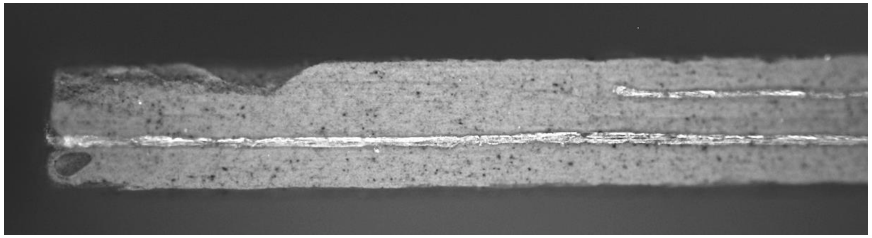
Your Kind Attention!

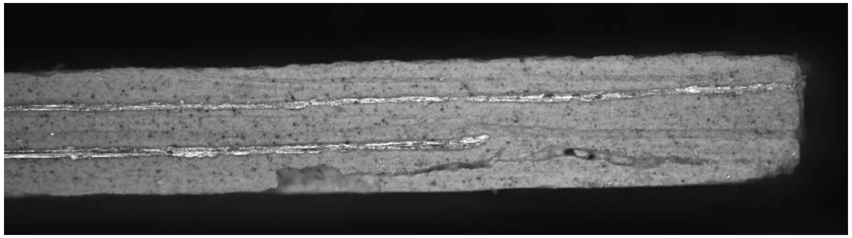
Co-Casting – The New Manufacturing Process



For film thicknesses < 50 µm
required green tape thicknesses: < 80 µm

Limit of accurately metallizing and stacking is reached





Co-casted piezoelectric ML with interdigital electrode structure

- Electrode thickness: 5-10 µm
- Ceramic layer thickness: 30-70 µm