LEAD-FREE PIEZOCERAMIC MATERIALS FOR INDUSTRIAL APPLICATIONS

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PIEZOTECHNOLOGY PI

Physik Instrumente (PI): Worldwide

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Standorte für Entwicklung, Fertigung, Vertrieb und Service
- PI Karlsruhe
- PI Ceramic
- PI miCos

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- PI Japan
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- PI Singapore
- PI Korea

PIEZOTECHNOLOGY

- **PI Ceramic founded in 1992 as a subsidiary of Physik Instrumente (PI)**
- **Based in Lederhose, Thuringia, Germany**
- **Staff: 200**

Legal situation

State of the Art: Lead-free materials

BNT-based materials

Conclusion

RoHS

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- **RoHS** – Restriction of the use of certain hazardous substances
- EU Directive 2002/95/EG since 01.07.2006 (RoHS I)
- Since 03.01.2013 replaced by:
- EU Directive 2011/65/EU (RoHS II)

Verbotene Stoffe gemäß Artikel 4 Absatz 7 und zulässige Höchstkonzentrationen in homogenen Werkstoffen in Gewichtsprozent

Blei (0,1%)

Quecksilber (0,1%)

Cadmium (0,01%)

Sechswertiges Chrom (0,1%)

Polybromierte Biphenyle (PBB) (0,1%)

Polybromierte Diphenylether (PBDE) (0,1%)

RoHS

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- All EEE categories included
- Exemption (Annex III: 7c) „Lead in piezoelectric ceramics"
- Exemption (Annex IV: 14) „Lead in single crystal piezoelectric materials for ultrasonic transducers"

- No Exemption if there is lead-free solution
- Exemption's can be cancelled at any time
- Expiry, if there is no application for continuation

REACH

- Links to the REACH Regulation (1907/2006/EC)
- Registration, Evaluation, Authorization, Restriction of Chemicals
- Since January 2013

Lead oxid (Lead monoxid)
Lead tetroxid (orange lead)
Lead titanium trioxid
Lead Titanium Zirconium Oxid

- Listed in Annex XIV (SVHC List for authorization)
- SVHC “Substances with very high concern”
- In the moment not clear what are the consequences

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What we have to consider

- Raw Materials
- Oxides, Carbonates, Precursors, Polymers, Solvents
- REACH: yes

- Process and Production
- Mixtures, Calcinates, Precursors
- REACH: most probably yes

- Products, Components, Applications
- REACH: most probably no

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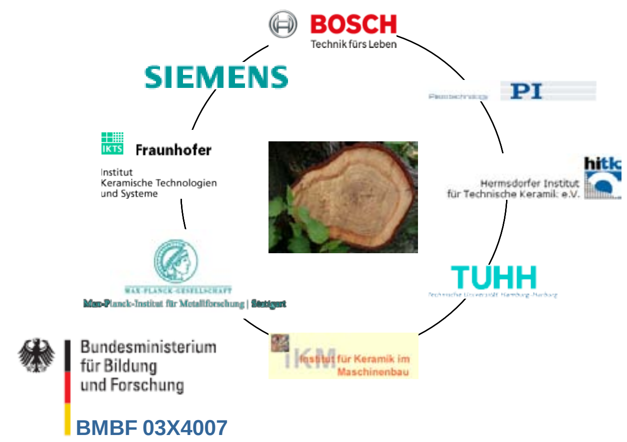
Lead-free materials

- 50 years of industrial use of PZT
- Since beginning of 1990´s restart of research, especially in Japan
- Today still extensive research activities worldwide
- In Germany since 2004: Industry-driven research activities
- PI Ceramic starts their own R&D activities in2004

Main goals:

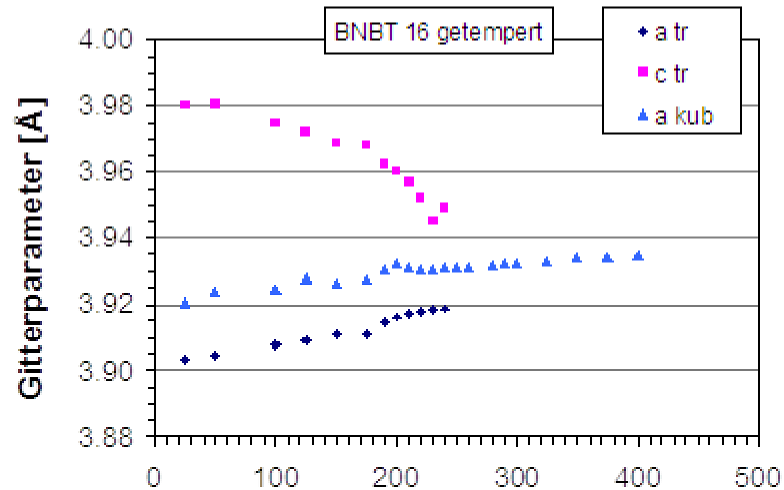
- **Investigation of promising compositions**
- **Working temperature range -40 to 150 °C**
- **BNT based compositions with MPB**
- **KNN – LTS and KNN – LT**
- **Investigation of technological routes**
- **Multilayer technology**
- **Texturization**
- **More than 400 compositions investigated**

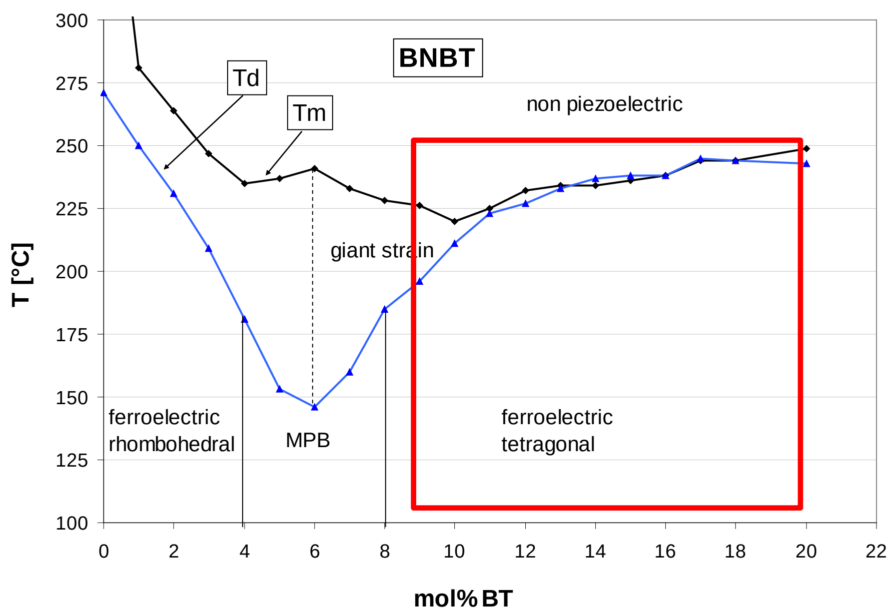
RealMAK-Consortium

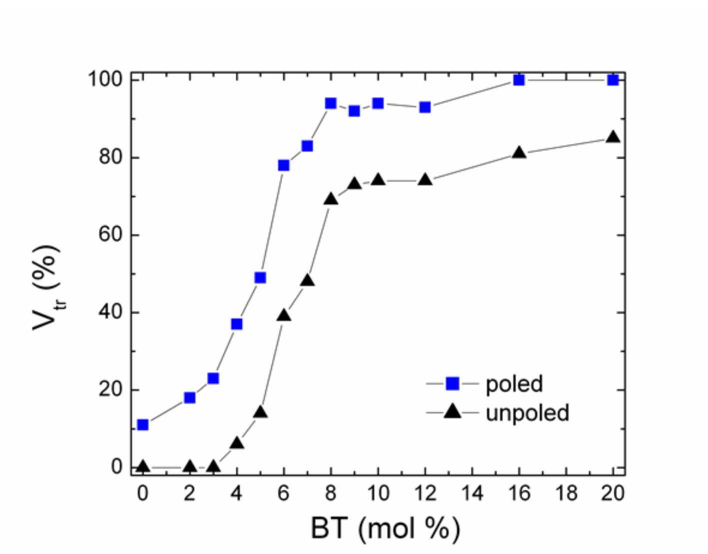


BNT-based materials

- Piezoelectric effect below T_d
- Phase transition at T_d
- Field induced phase transition during poling
- Giant strain behavior above T_d

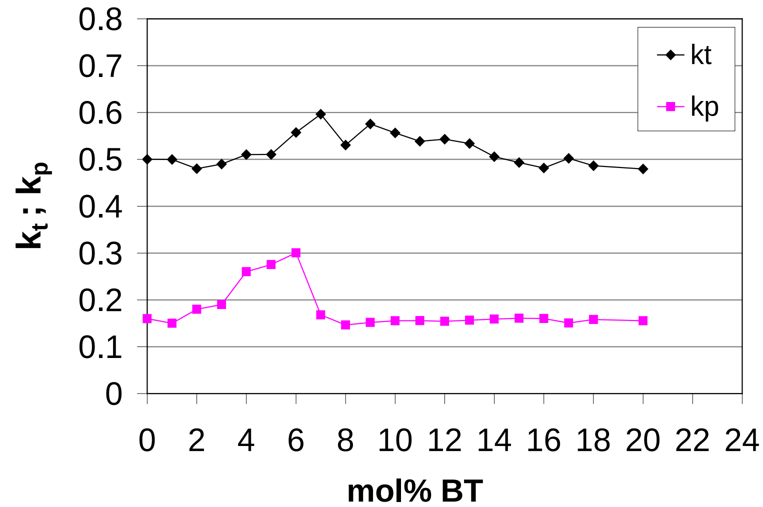


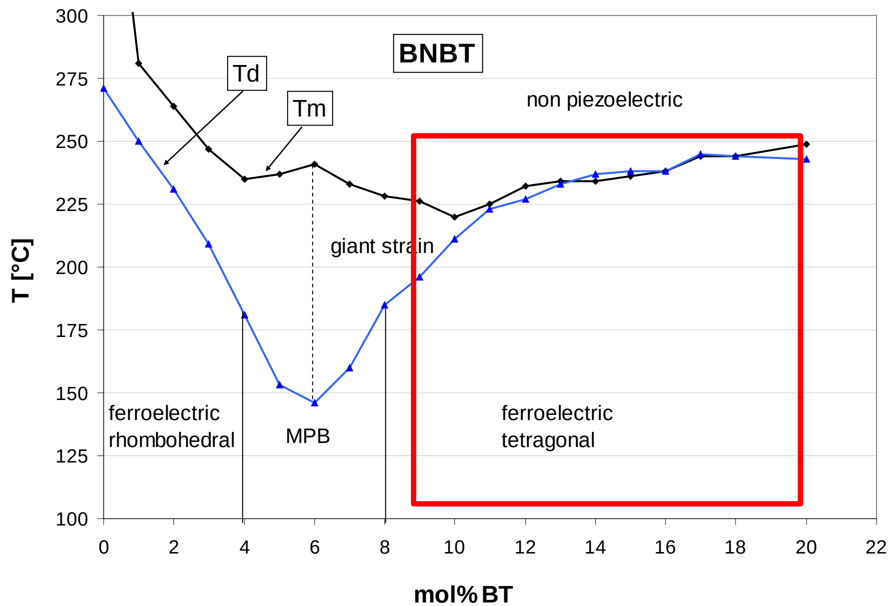


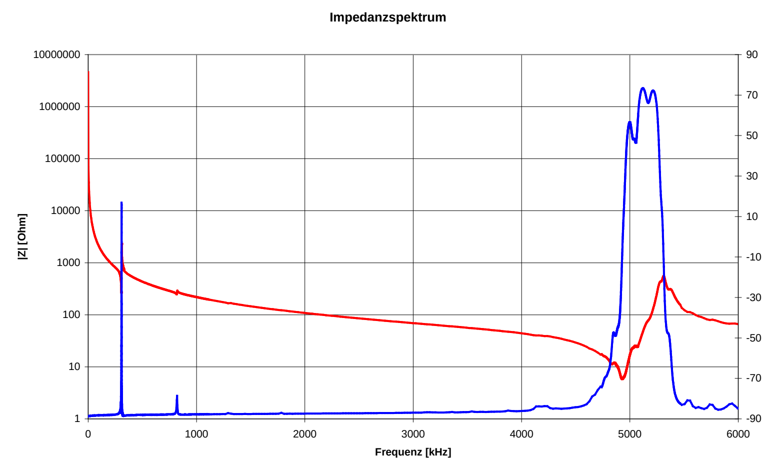


BNT-based materials

- Enhancement of the properties at the MPB
- Strong anisotropic materials







KNN-based materials: Modified by Li, Ta, Sb

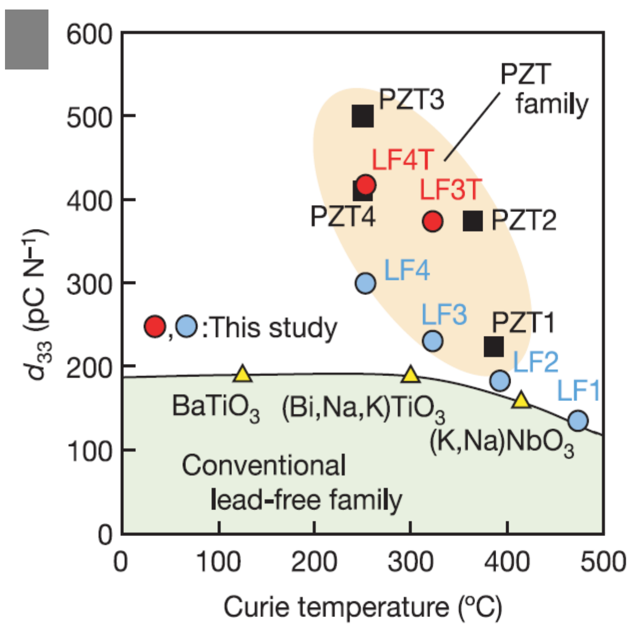
- (KNaLi)(NbTaSb)O3 based system (Saito et al., 2004)
- For textured material: Highest measured strain at RT so far
- Critical patent situation

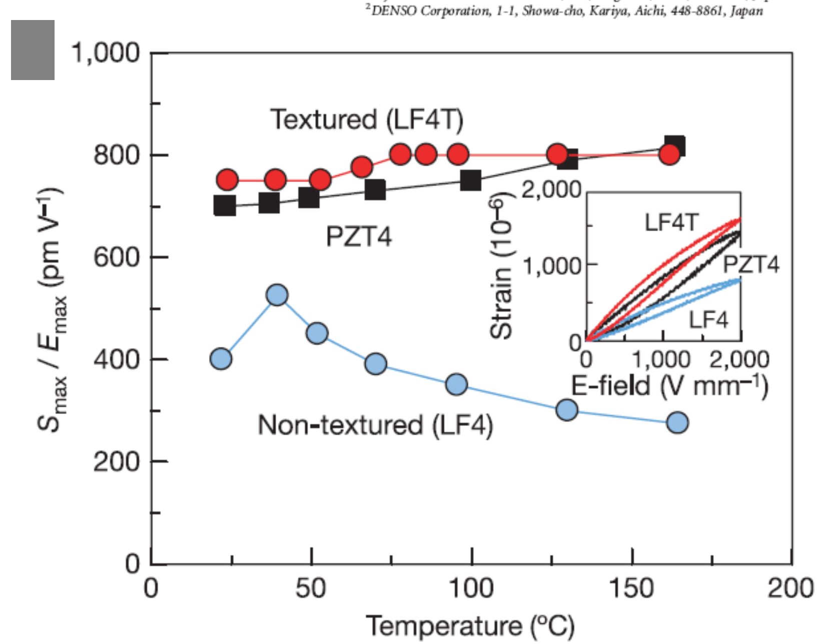
Letters to Nature 2004

Lead-free piezoceramics

Yasuyoshi Saito[1], Hisaaki Takao[1], Toshihiko Tani[1], Tatsuhiko Nonoyama[2], Kazumasa Takatori[1], Takahiko Homma[1], Toshiatsu Nagaya[2] & Masaya Nakamura[2]

[1] Toyota Central R&D Laboratories, Inc., Nagakute, Aichi, 480-1192, Japan
[2] DENSO Corporation, 1-1, Showa-cho, Kariya, Aichi, 448-8861, Japan





KNN-based materials: Modified by Li, Ta, Sb

- Phase transition temperature orthorhombic – tetragonal ($T_{O\text{-}T}$) determines performance vs. temperature behavior
- Position of $T_{O\text{-}T}$ strongly depends on composition (<RT - +220°C) -> heavy requirement on reproducibility and process stability
- High strain at room-temperature is not enough

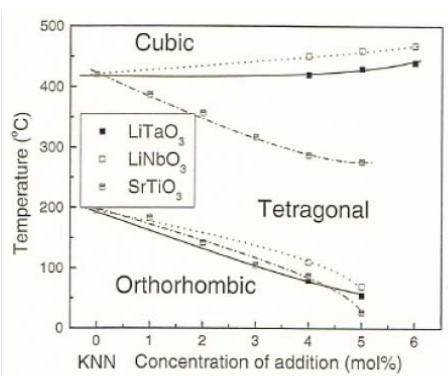
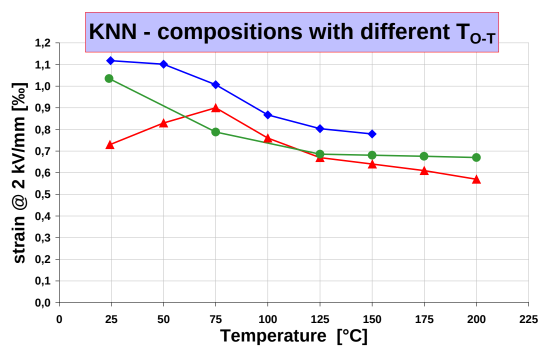
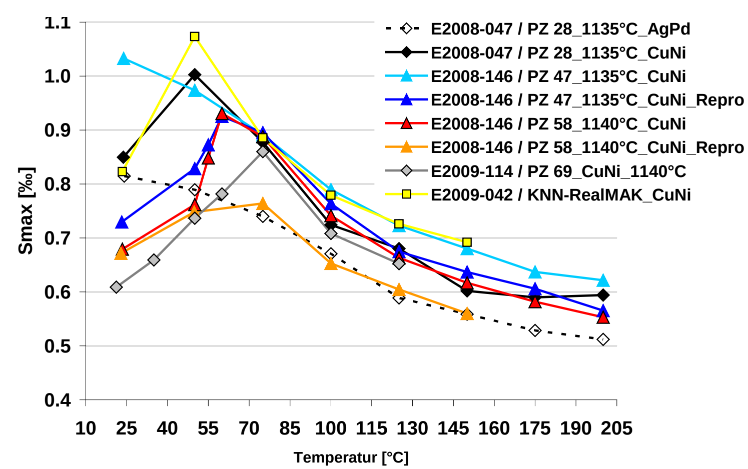


Fig. 14 Phase diagram for modified KNN (data from [8–11]) Note: $BaTiO_3$ additions are analogous to $SrTiO_3$ [9]

Shrout, Zhang
J. Electroceram. 2007

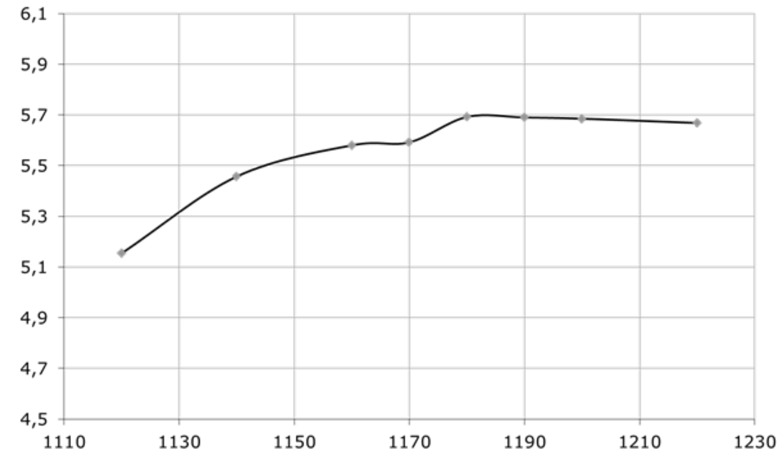




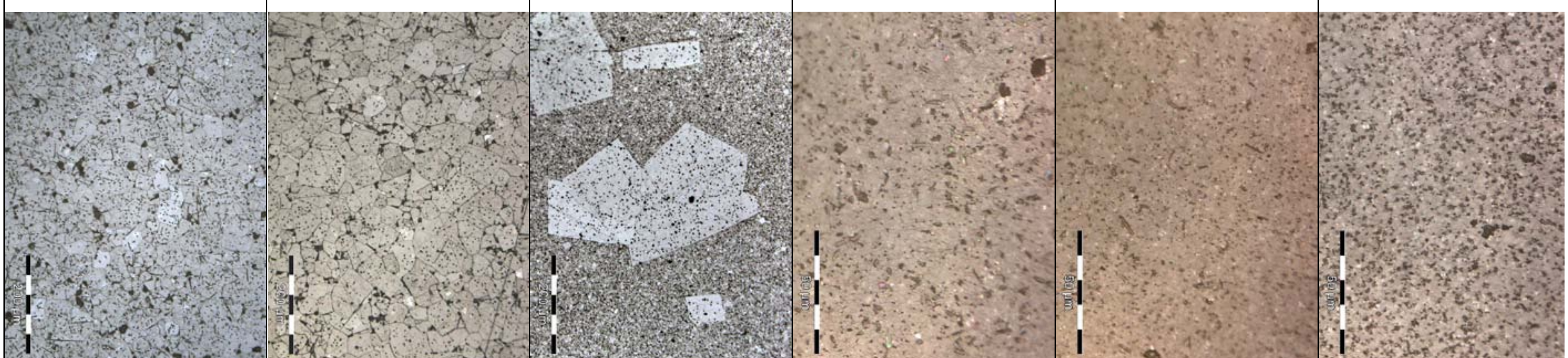
Future Tasks – Technology Development

BNT-based materials

- Sintering behavior
- Density vs. sintering temperature
- Microstructure development



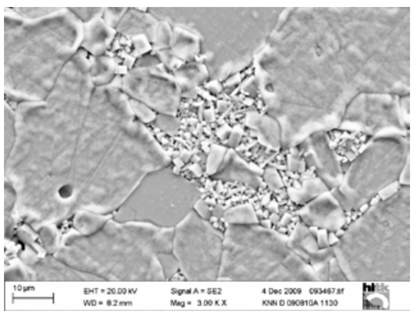
1220 °C	1200 °C	1180 °C	1160 °C	1140 °C	1120 °C

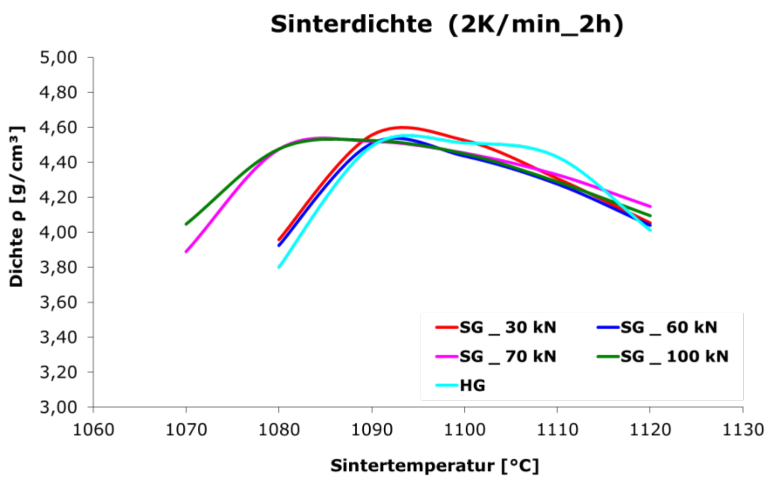


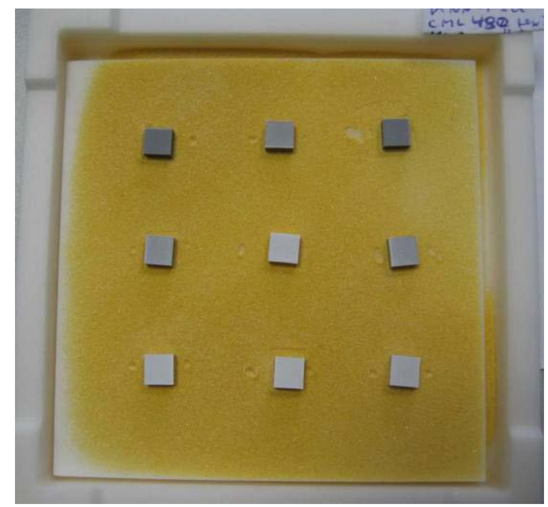
Future Tasks – Technology Development

KNN-based materials: Modified by Li, Ta, Sb

- KNN difficult to densify
- heavy requirement on reproducibility and process stability







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BNT-based materials

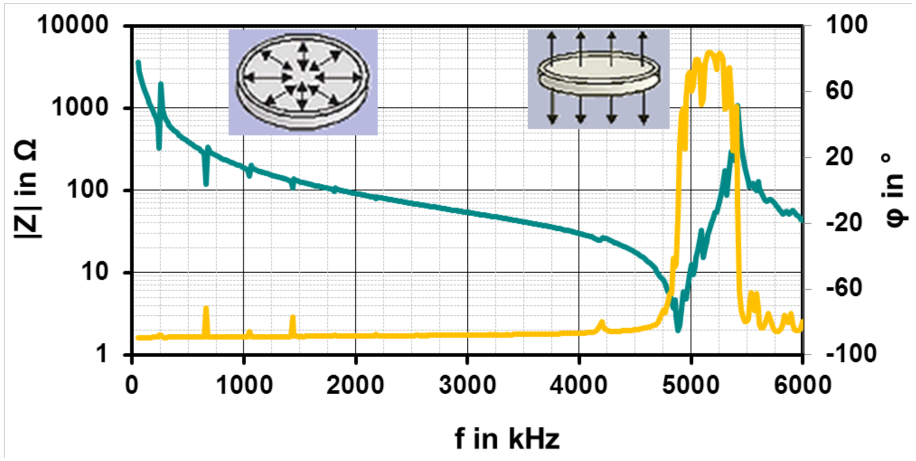
- Conventional mixed-oxide technology

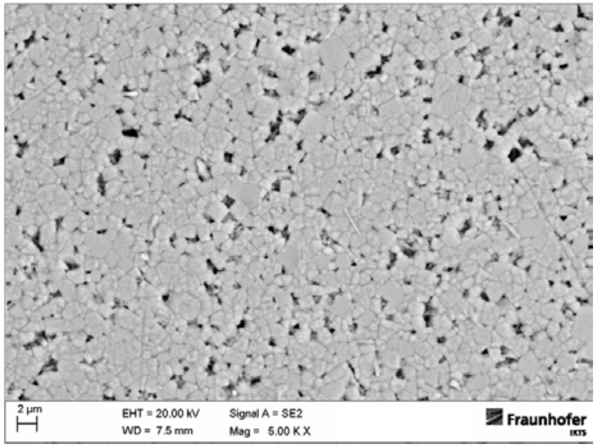
Mixing	Reagent grade metal oxide and carbonate powders in isopropanol using a disk mill
↓ Calcining	850°C - 950°C
↓ Milling	in isopropanol using a disk mill
↓ Granulating	
↓ Pressing	uniaxial press
↓ Sintering	1120°C - 1220°C

BNT-based Lead-free materials

BNT-based materials

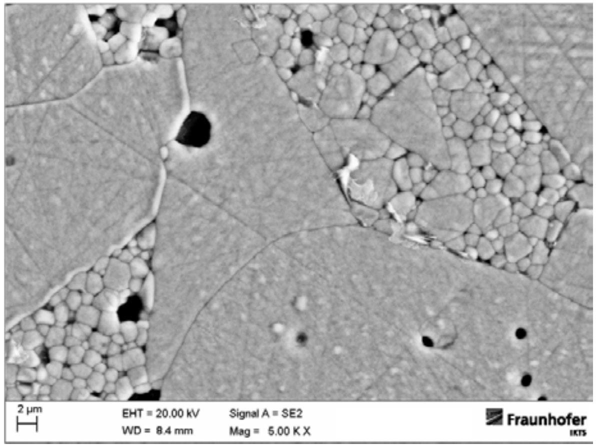
- Strong anisotropic $K_t >> K_p$
- Different microstructure





Homogeneous, fine grained

Grain size ≤ 2 µm

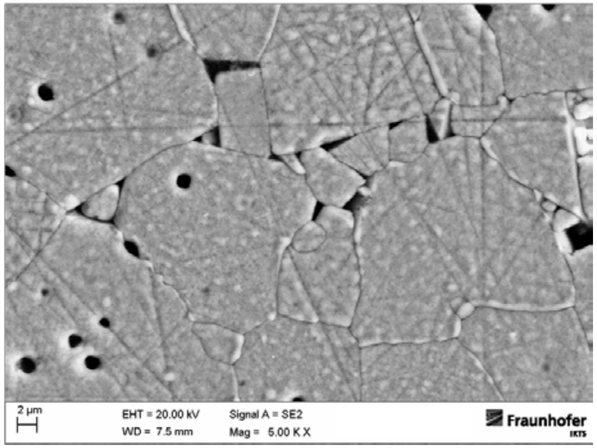


Abnormal grain growth

Very inhomogeneous

Grain size up to 300 µm

High intragranular porosity

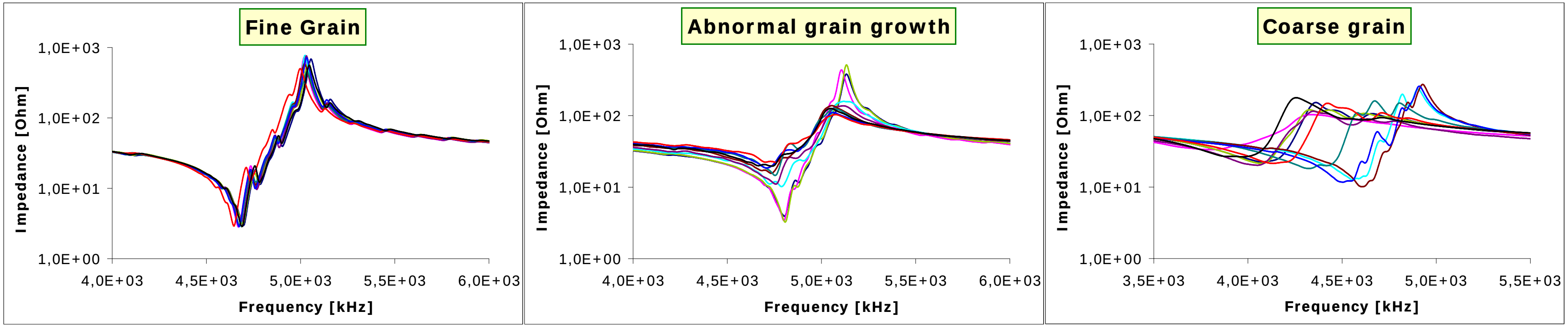


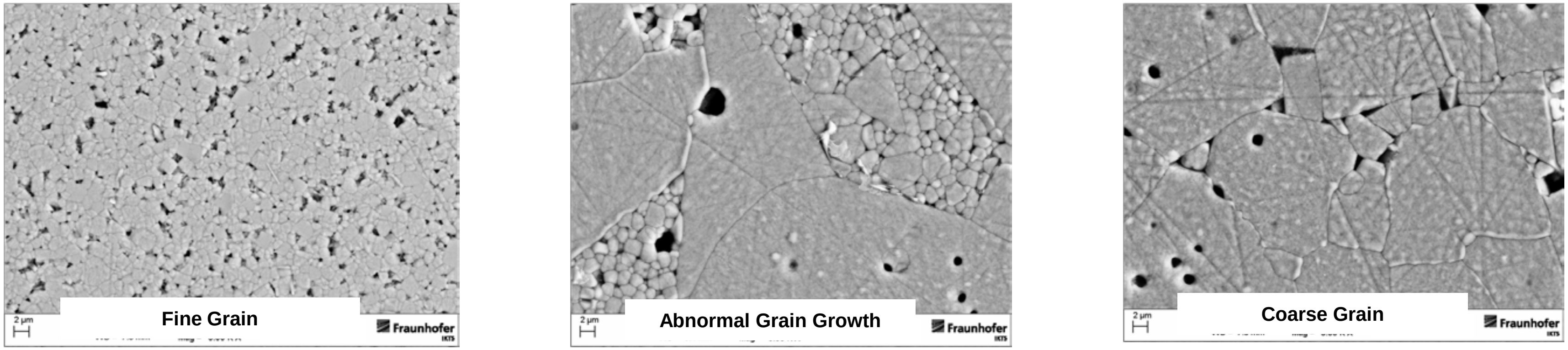
Homogeneous, coarse grained

Grain size around 50 µm

Intergranular porosity

Microstructure dependence of the thickness mode vibration





Requirement for a stable manufacturing process:

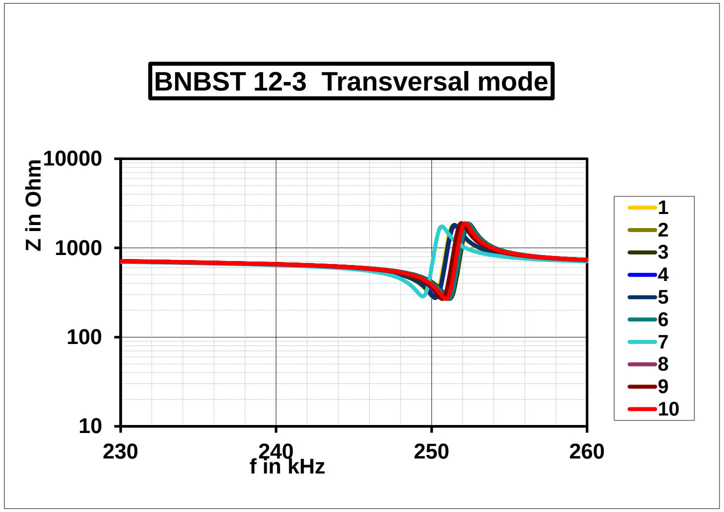
Control of microstructure

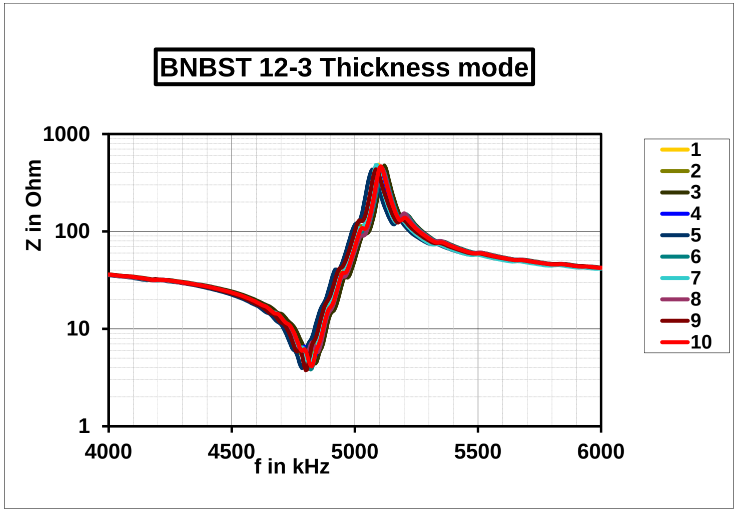
“Small signal” characterization

Small signal parameters (typical)

- Preliminary data PIC 700

Parameter		BNT based
		BNBST
T_d	[°C]	~200
$\varepsilon_{33} / \varepsilon_0$		700
$\varepsilon_{11} / \varepsilon_0$		570
tan δ $[10^{-3}]$		20
d_{33}	[pm/V]	120
d_{31}	[pm/V]	-40
d_{15}	[pm/V]	110
k_p		(0,15)
k_t		0,4
k_{33}		0,4
k_{31}		(0,14)
k_{15}		0,3





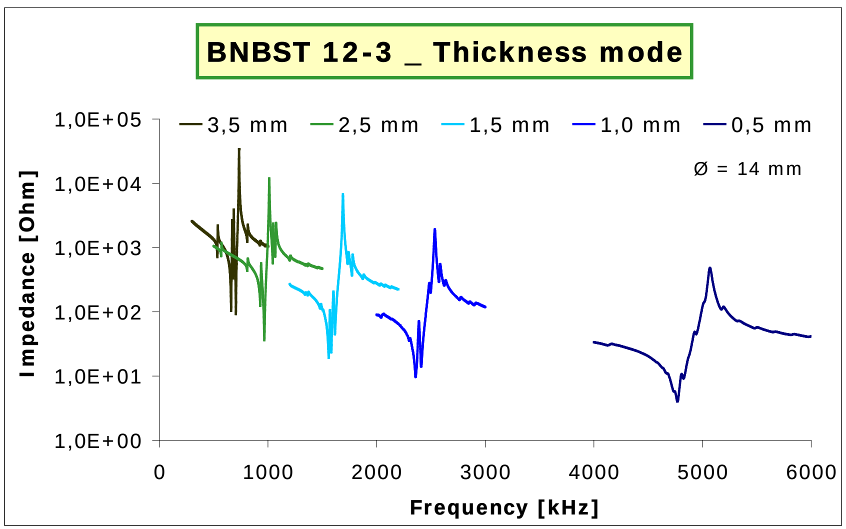
Thickness dependence

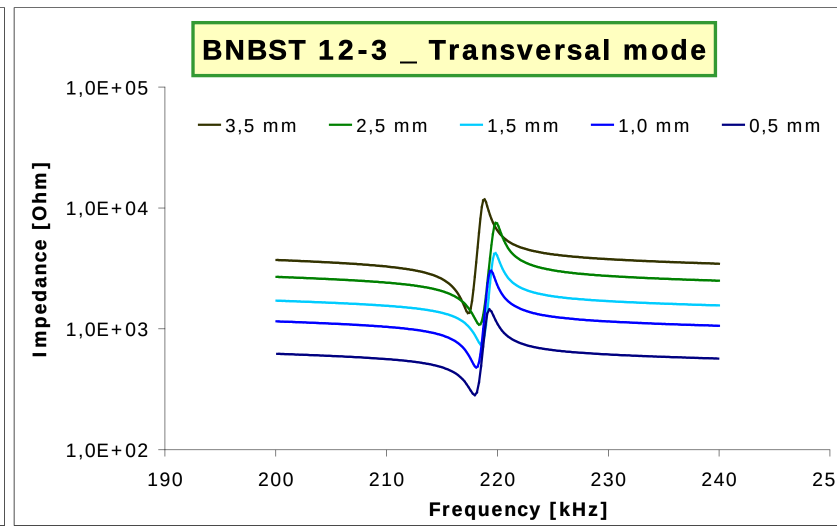
Impedance curves of discs with different thicknesses from 0,5 to 3,5 mm

Thickness mode: pure signal vibration at small thickness

strong coupling of different modes with increasing the thickness

Radial mode: value of the impedance increases with the thickness

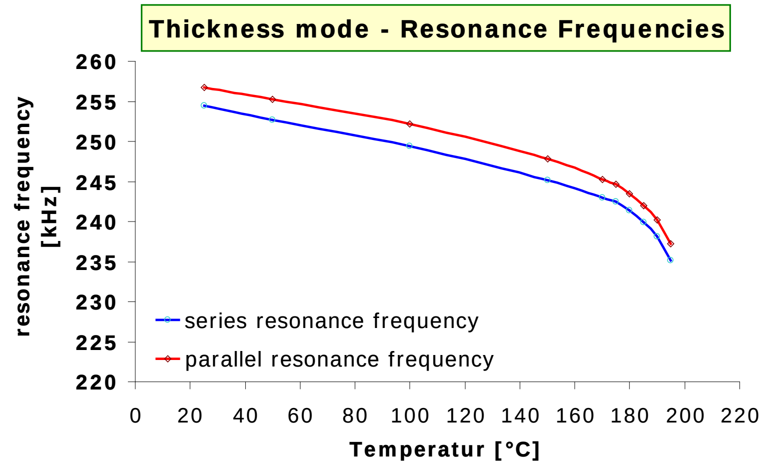


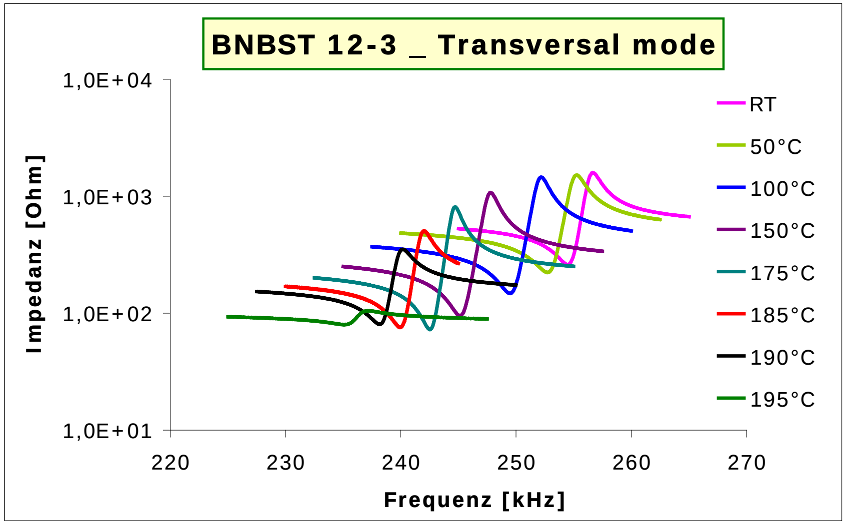


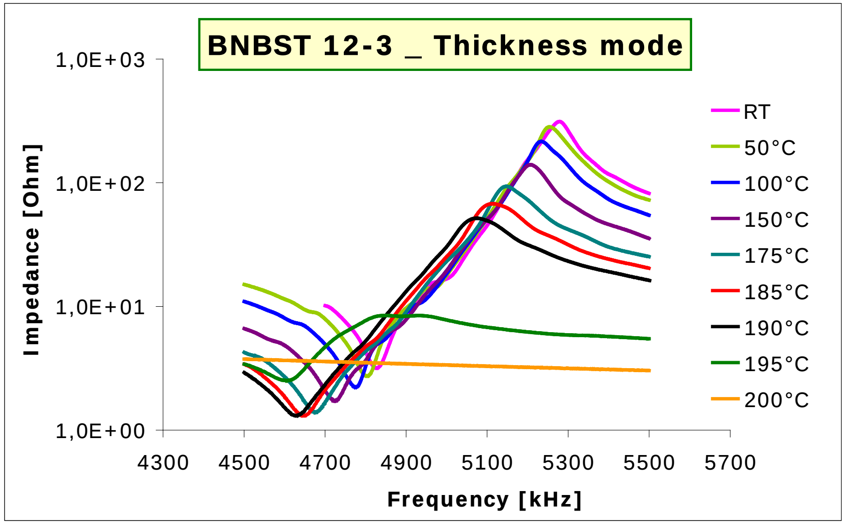
"Small signal" characterization

Temperature dependence

- Good stability up to T_d
- at T_d resonance behavior disappears within 10K
- with increasing temperature the resonance shifts to lower frequencies

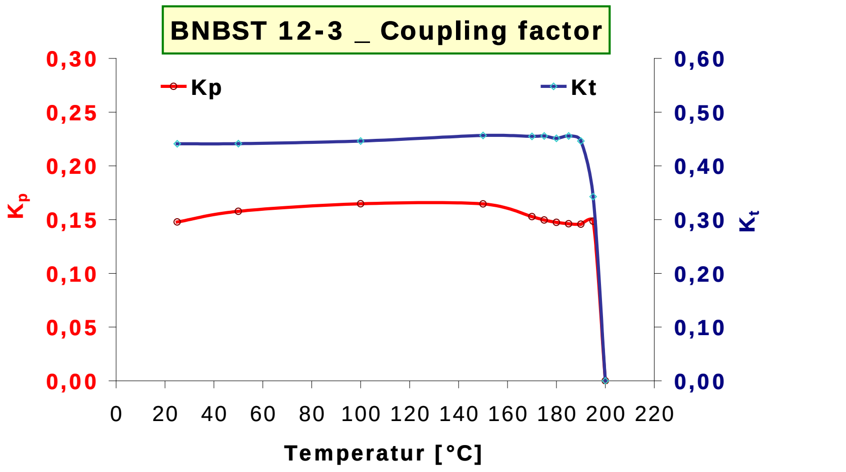


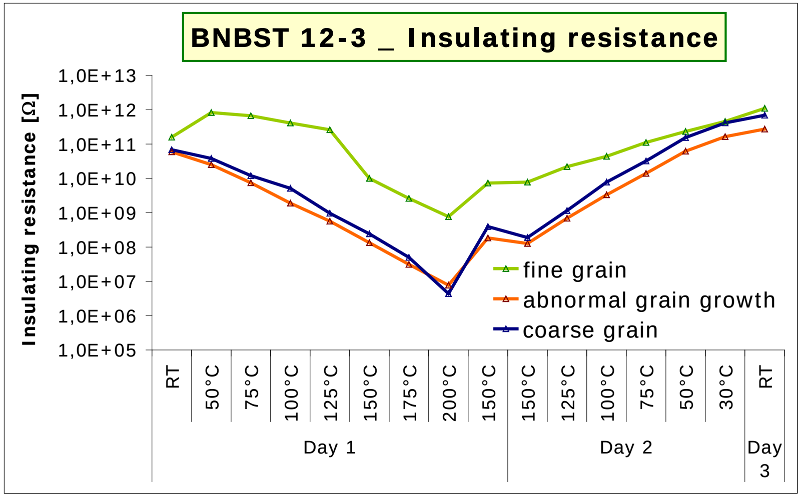


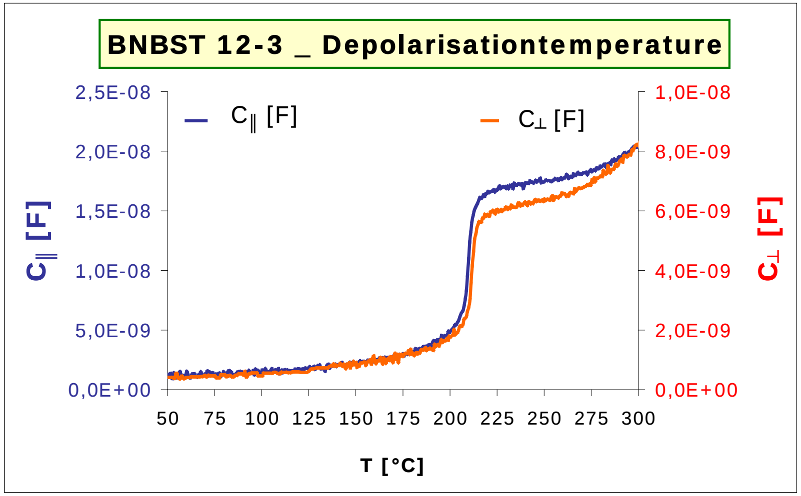


Temperature dependence

- Good stability up to T_d
- High insulation resistance with homogeneous fine-grained microstructure
- T_d: no differences between $C_{\parallel}$ and $C_{\perp}$

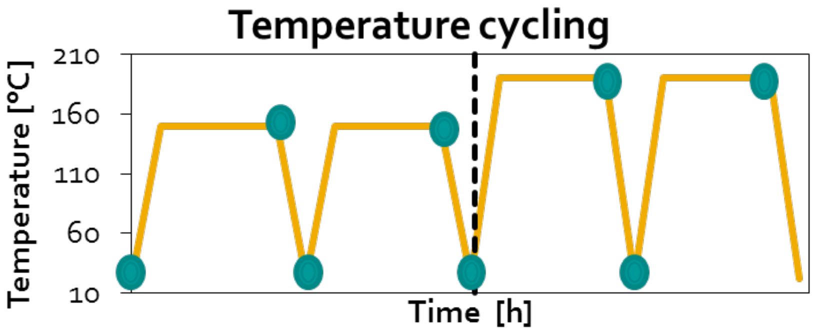


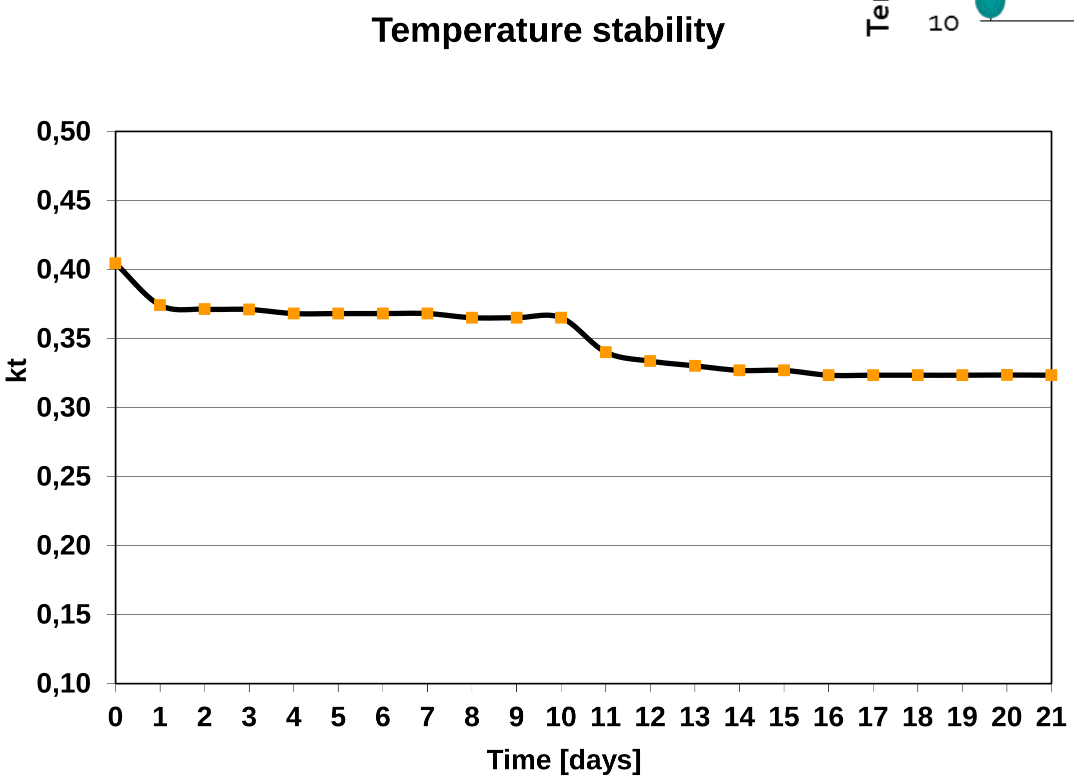




Temperature stability

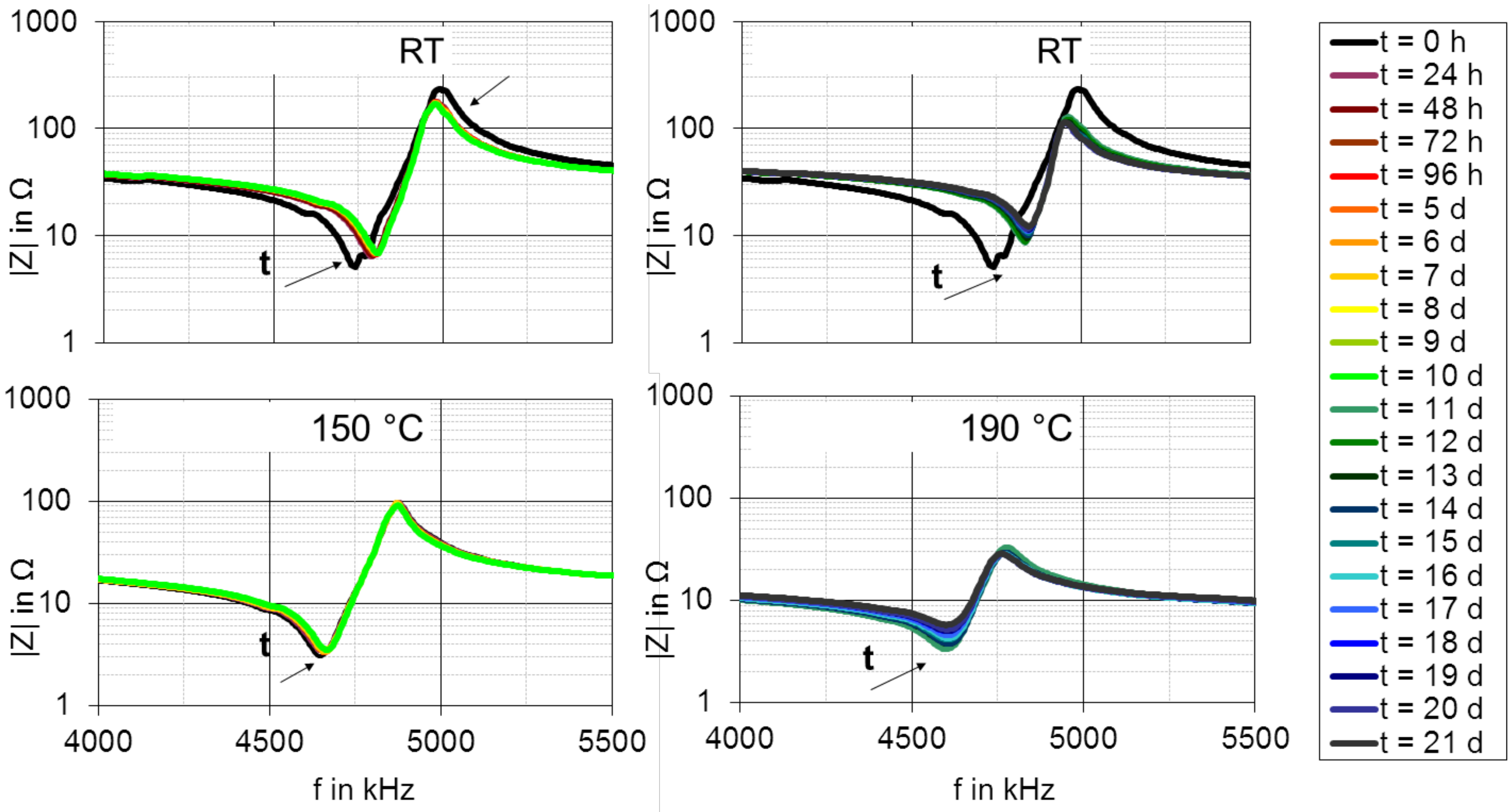
- K_t at RT after temperature cycling
- Good stability up 150 °C





Temperature stability

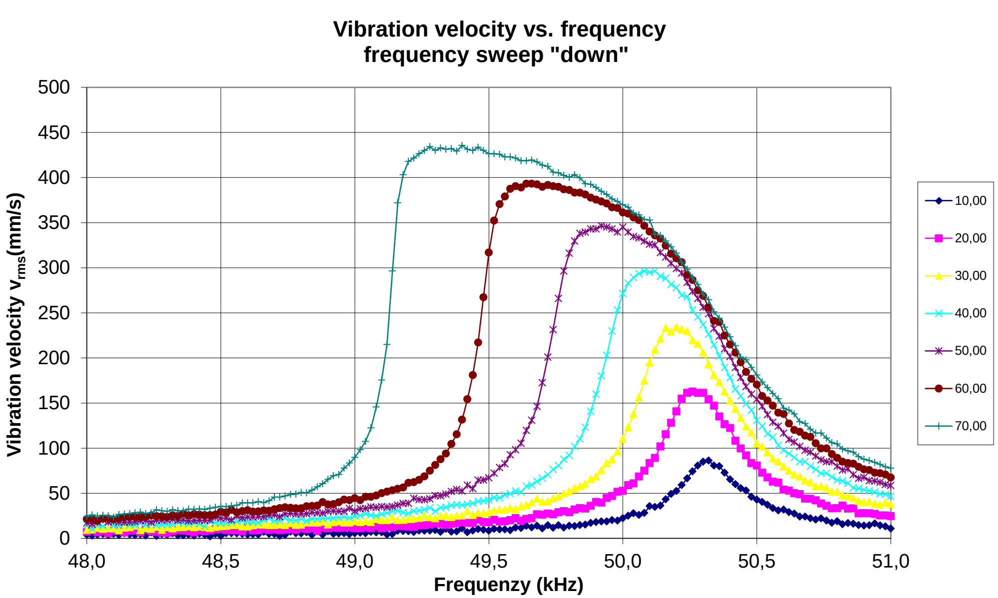
- Impedance curves
- Good stability up 150 °C



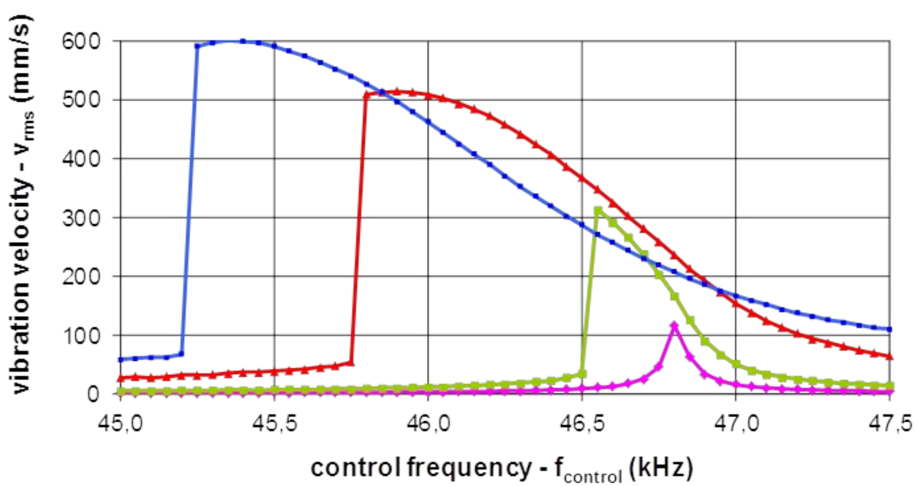
Large signal resonance behavior of BNBST 12-3

- Vibration velocity 10 to 70 v_{rms} (BNBST 12-3)
- Vibration velocity 0,1 to 10 v_{rms} (hard PZT)
- v_{max} ~ 430 mm/s @ 70V and v_{max} ~ 600 mm/s @ 10V
- No jump behavior for BNBST 12-3

BNBST 12-3

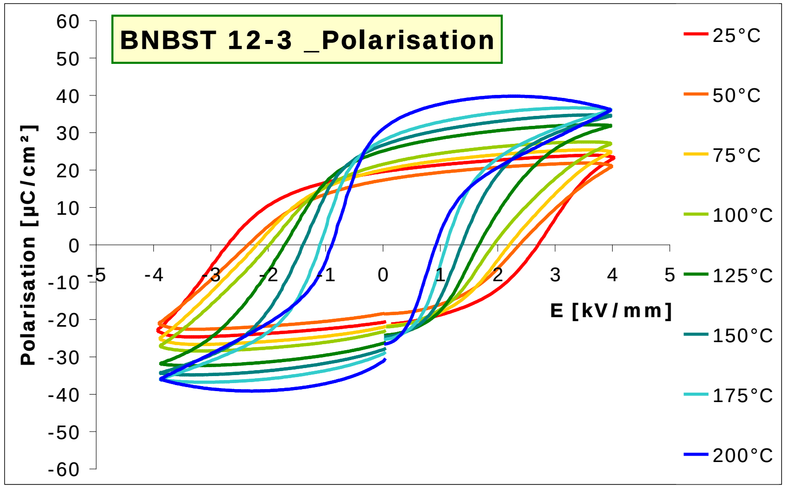


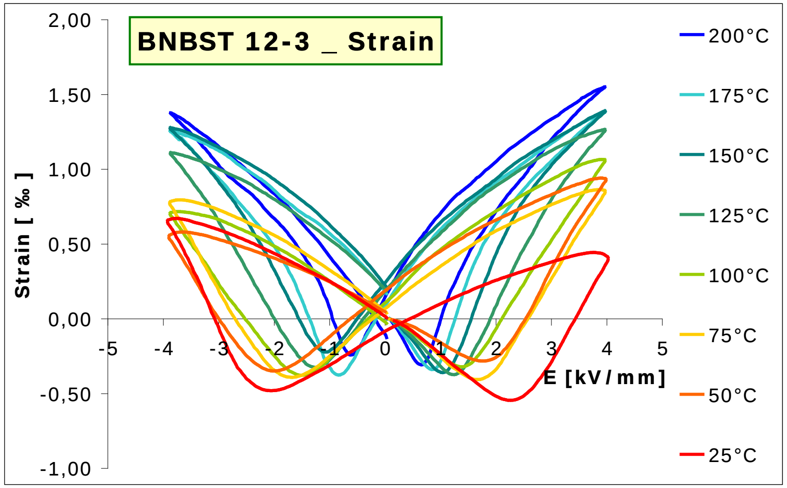
Hard PZT

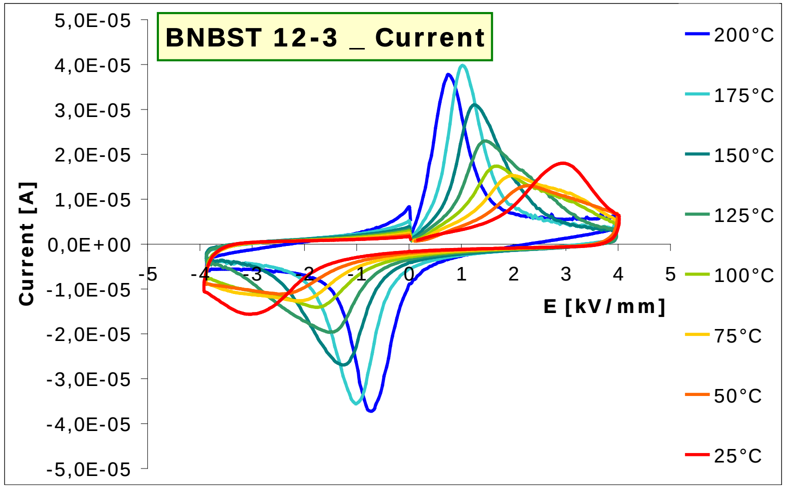


Bipolar hysteresis

- Increase of the strain with increasing temperature
- Increase of the polarization with increasing temperature
- Decrease of the coercive field strength with increasing temperature



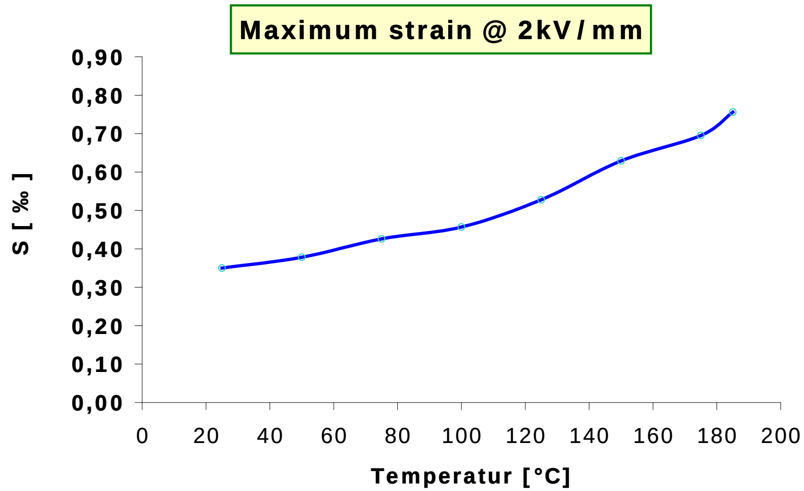


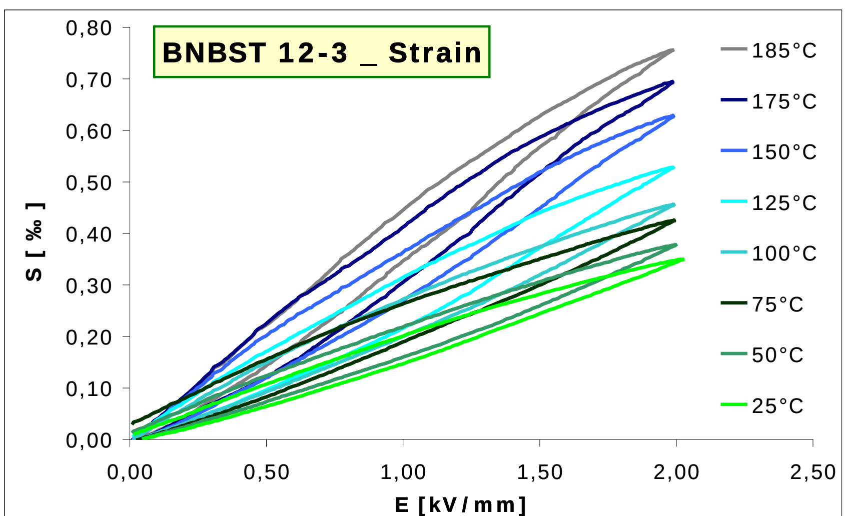


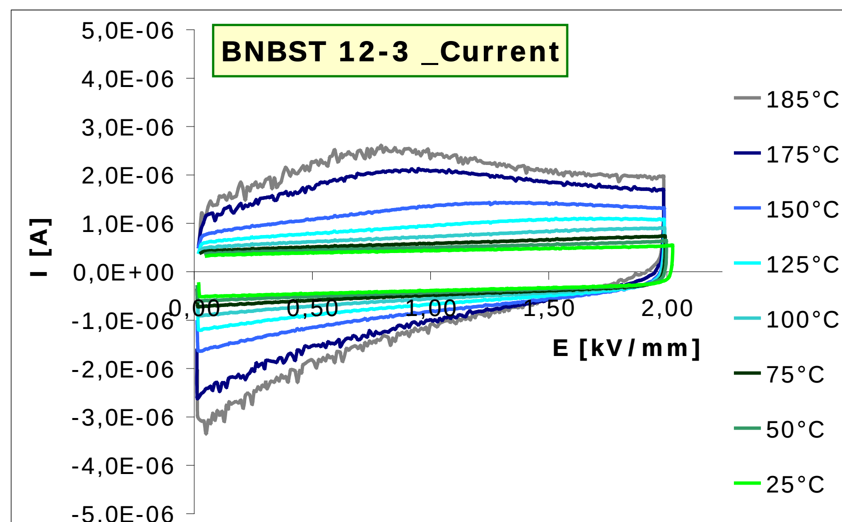
"Large signal" characterization

Unipolar hysteresis

- Strong increase of unipolar strain with temperature up to T_d
- Low conductivity up to 150 °C







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State of the Art: Lead-free materials

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Conclusion

Conclusions

- Standard PZT materials: Typical Properties

Parameter		Soft PZT		Hard PZT	
Common		PZT 5A	PZT 5H	PZT 4	PZT 8
MIL		DOD II	DOD VI	DOD I	DOD III
EN 50324-1		200	600	100	300
T_C	[°C]	≥330	≥ 190	≥ 310	≥ 290
$\varepsilon_{33} / \varepsilon_0$		1800	≥ 3500	1300	1300
tan δ [10^{-3}]		20	20	4	4
d_{33}	[pm/V]	400	600	290	220
k_p		0,58	0,60	0,56	0,51
Q_m		80	65	500	1000

Conclusions

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- Lead-free materials: Typical Properties

Parameter		BNT based		KNN based	
		BNBST	BNBST (MPB)	KNN - LTS	KNN - LT
T_C / T_d	[°C]	200	< 150	≥310	≥290
ε_{33} / ε_0		700	1000	1300	1200
tan δ [10^{-3}]		30	30	30	30
d_{33}	[pm/V]	120	150	(300)	(250)
k_p		0,15	0,30	0,35	0,35
Q_m		200			

- No lead-free composition matches the standard characteristics

Conclusions

- No adequate replacement for PZT until now (and the next 10 - 15 years?)
- Special Lead-free solutions are expected

- BNT-BT based materials are promising for transducer and sensor applications
- KNN-based materials are promising for actuators
- Knowledge of the material properties under different working conditions
- Stable technologies for production necessary
- Tests in different applications necessary
- Samples of PIC 700 available

PI

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RealMAK

BMBF 03X4007

DelLead

BMBF 03X4002

The authors are responsible for the content

Thank you for your Attention!

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