Ferroelectric Properties of Lead-Free Ceramics Prepared by Solid-State Synthesis

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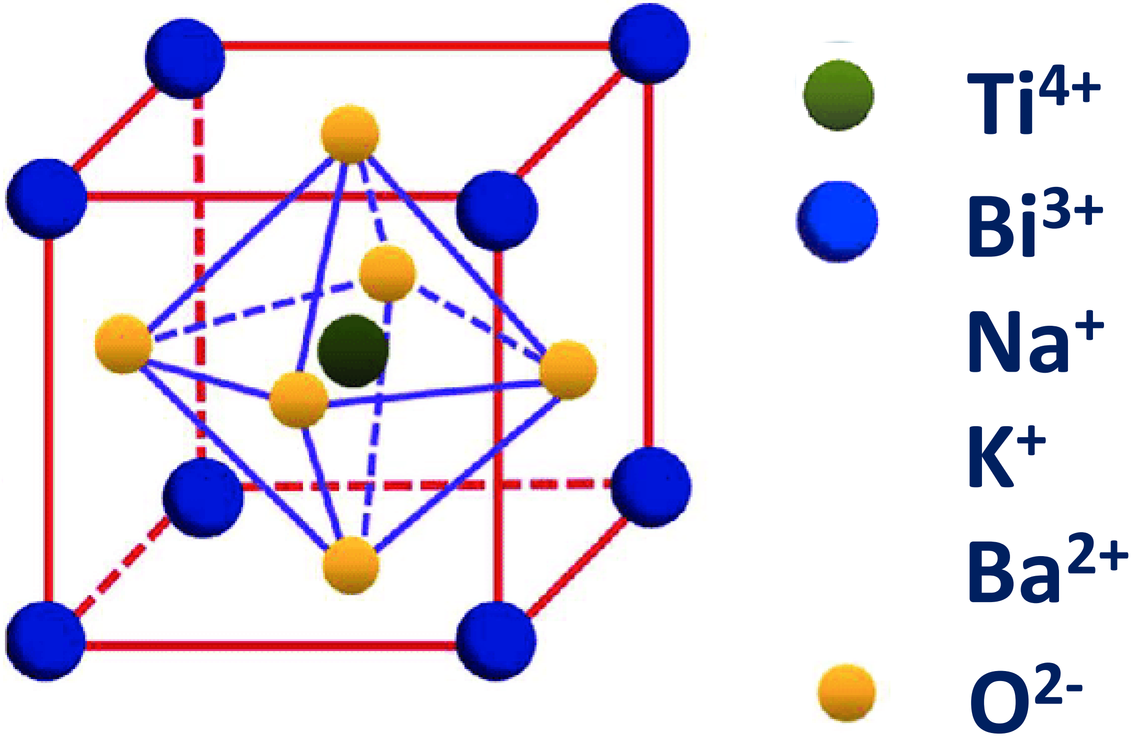
2nd July 2025
Faculty of Science, Zagreb

Perovskite structure

ABO_3



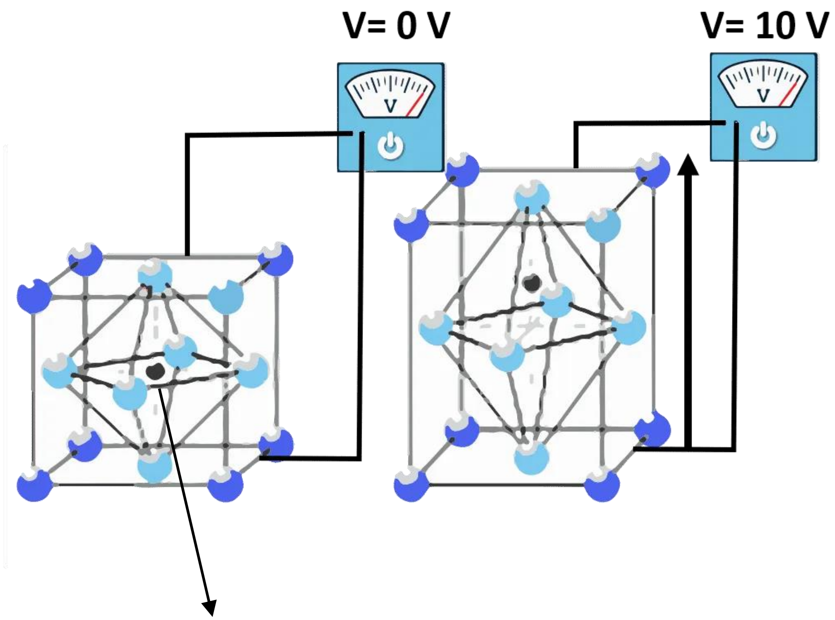
NBT-20KBT $0,8((Na_{0.5}Bi_{0.5})TiO_3)$ $0,2(K_{0.5}Bi_{0.5}TiO_3)$

NBT-5KBT-5BT $0,90((Na_{0.5}Bi_{0.5})TiO_3)$ $0,05(K_{0.5}Bi_{0.5}TiO_3)$ $0,05\ (BaTiO_3)$

NBT-8KBT-4BT $0,88((Na_{0.5}Bi_{0.5})TiO_3)$ $0,08(K_{0.5}Bi_{0.5}TiO_3)$ $0,04\ (BaTiO_3)$

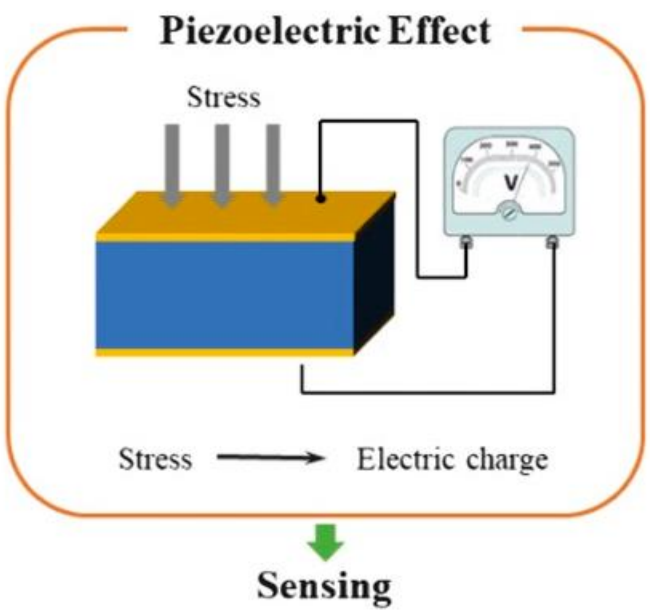
Piezoelectricity and ferroelectricity

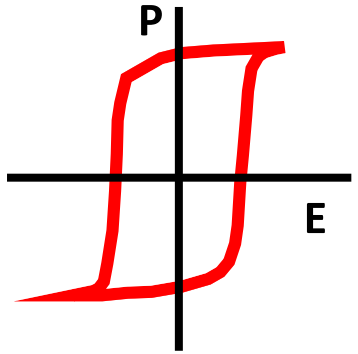
Mechanical stress ⇆ charge generation



No centre of symmetry=no piezoelectric properties

Piezoelectric factor or simply d_{33} (pC/N)



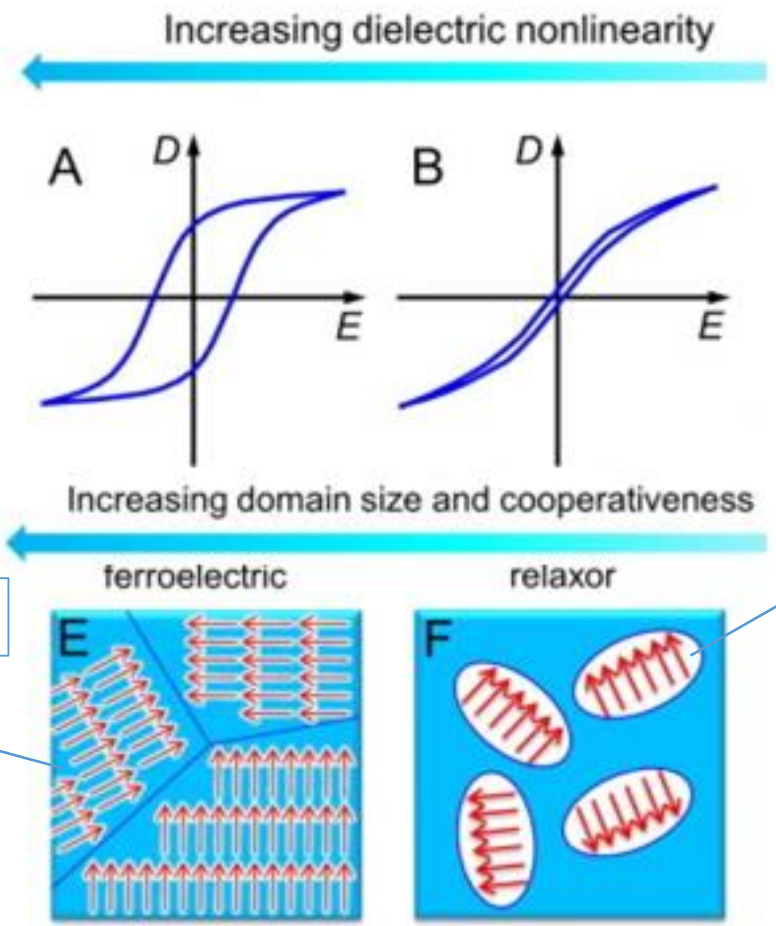


Ferroelectricity

-spontaneous polarization

-dipole moments→reversible with aplied electric field

Ferroelectrics vs relaxors

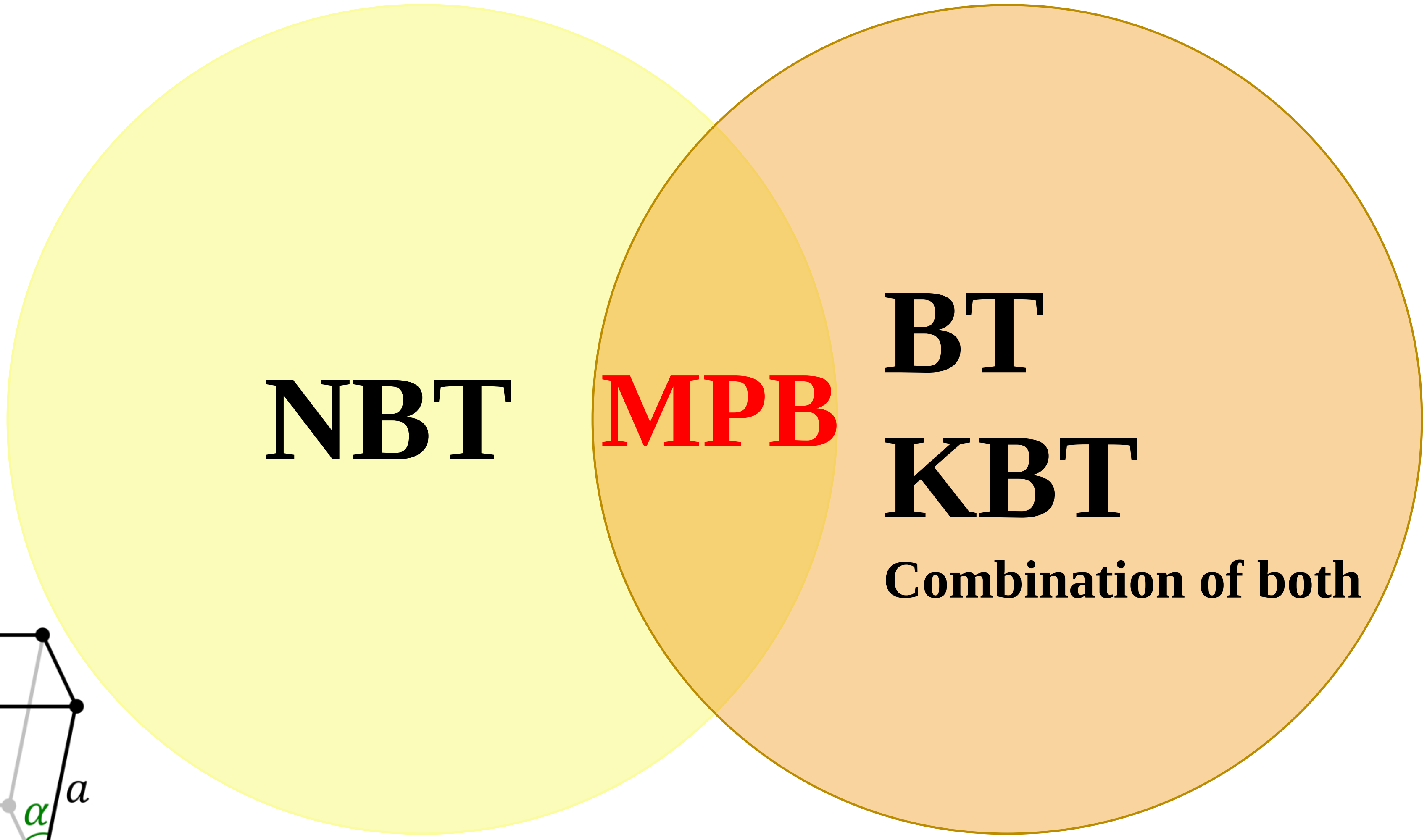


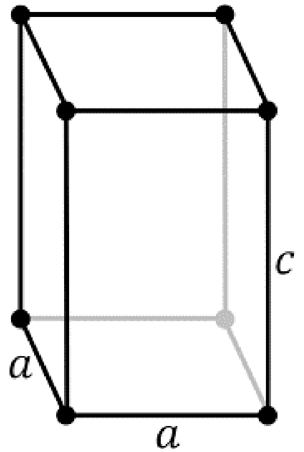
domains with long range order

PNRs=polar nano regions

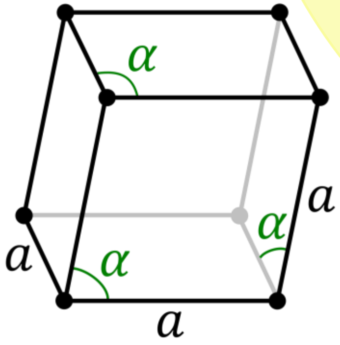
Rojac et al. **Commun. Mater.** 4 (2023) 12
Fan et al. **J Materiomics.** 7 (2021) 508-544

Solid solution (NBT-KBT)



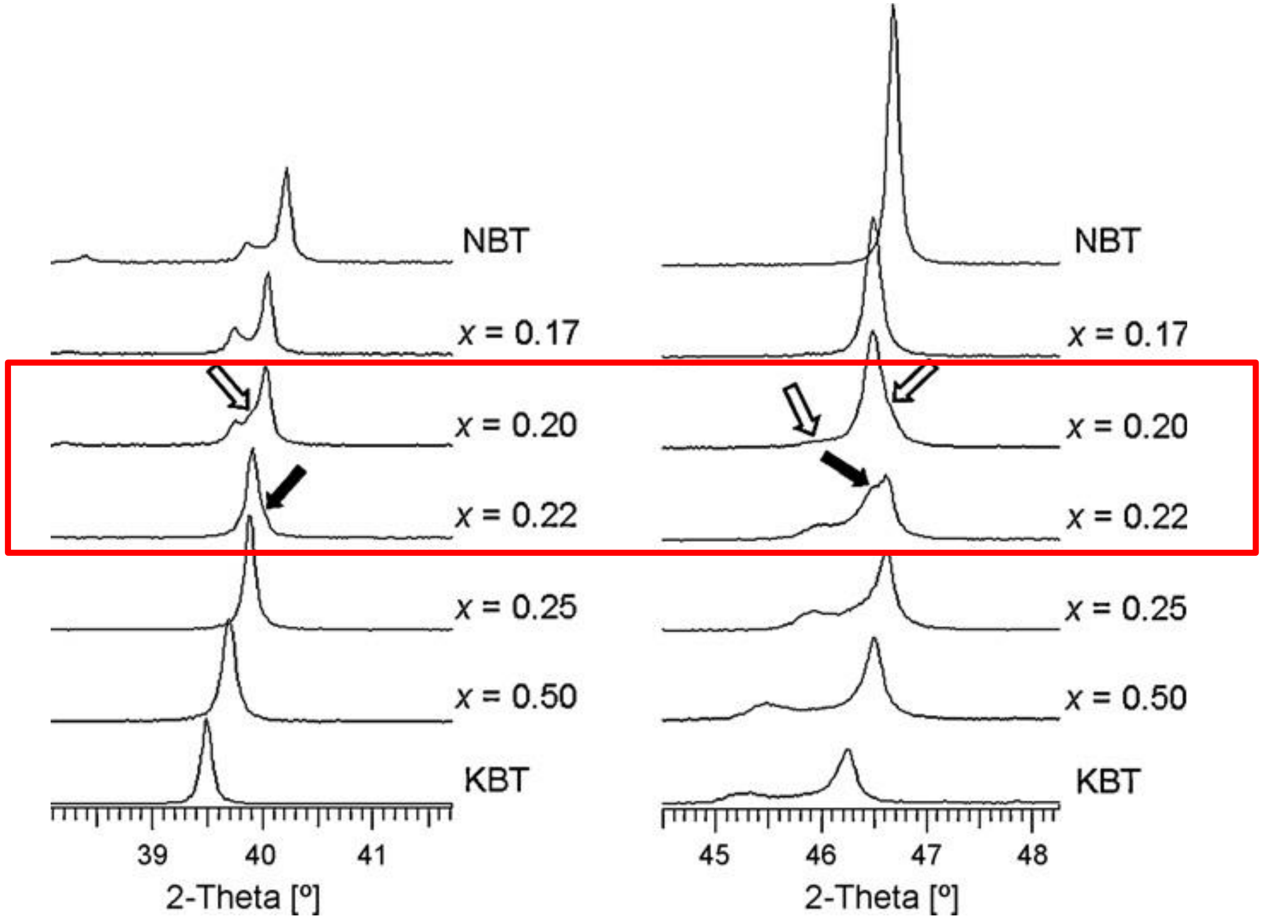


tetragonal

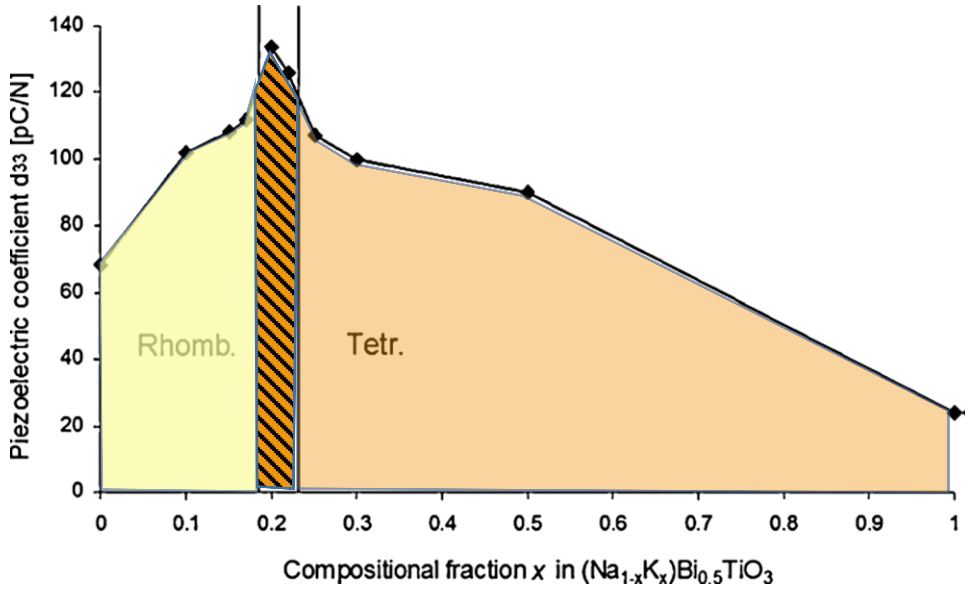


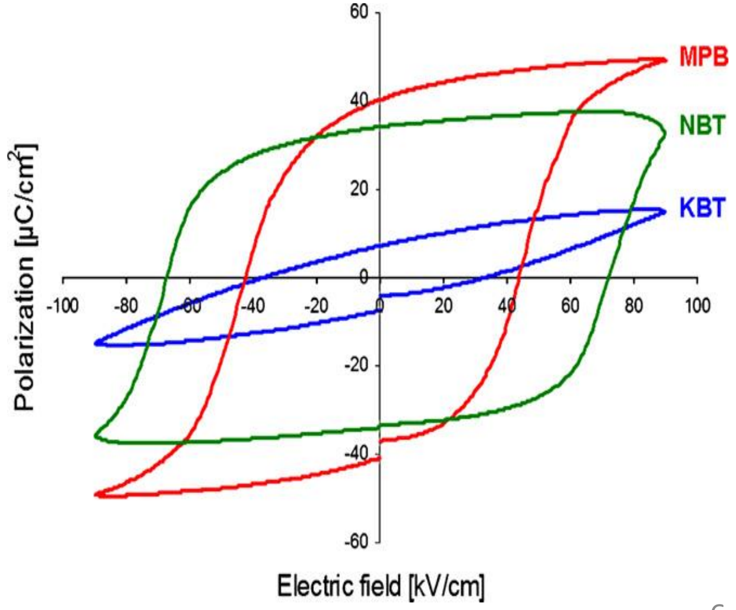
rhombohedral

NBT-20KBT $0,8((Na_{0.5}Bi_{0.5})TiO_3)$ $0,2(K_{0.5}Bi_{0.5}TiO_3)$

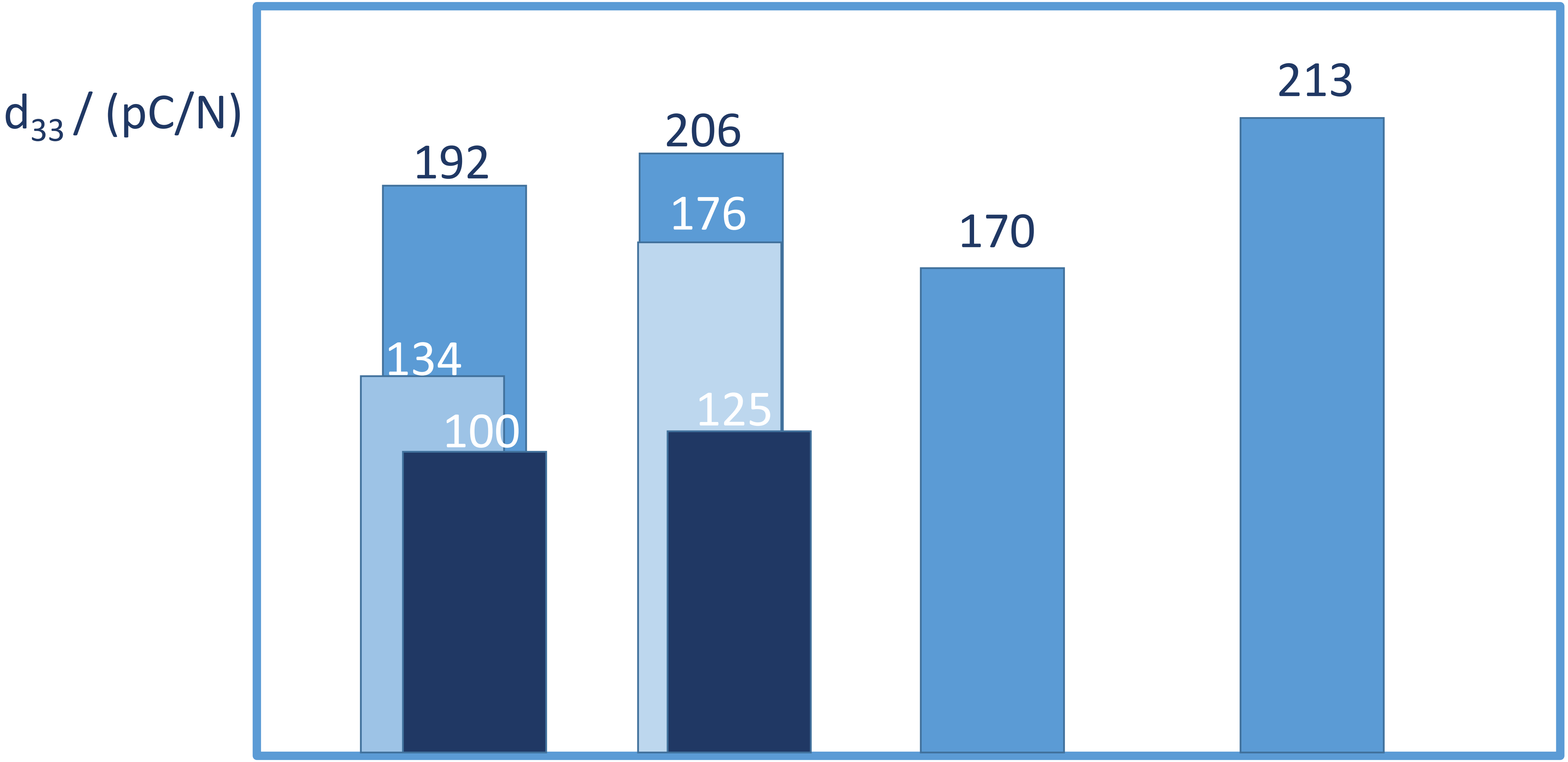


MPB





Otoničar et al. **J. Eur. Ceram. Soc**. 30 (2010) 971–979



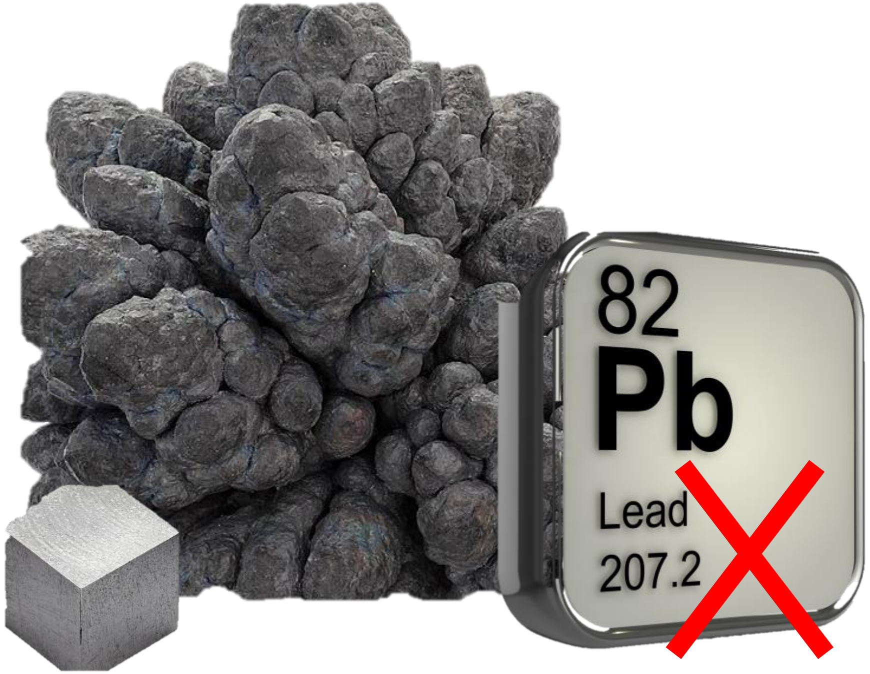
NBT-20KBT	NBT-BT	NBT-8KBT-4BT	NBT-5KBT-5BT
Zhang et al **J. Am. Ceram. Soc.** 91 (2008) 2716–2719	Sundari et al., **IOP Conf. Ser.: Mater. Sci. Eng**. 43 (2013) 012010	S.J. Zhang et al.,**Ultrason. Ferroelectr. Freq. Control** 54 (5) (2007) 910	Li et al **J. Alloys Compd.** 613 (2014) 181–186
Otoničar et al. **J. Eur. Ceram. Soc**. 30 (2010) 971–979	Chen et al. **J. Eur. Ceram. Soc**. 28 (2008) 843–849		
T. Takenaka et al., **Jpn. J. Appl. Phys.** 30 (9B) (1991) 2236.	Sasaki et al., **Jpn. J. Appl. Phys**. 38 (1999) 5564.		

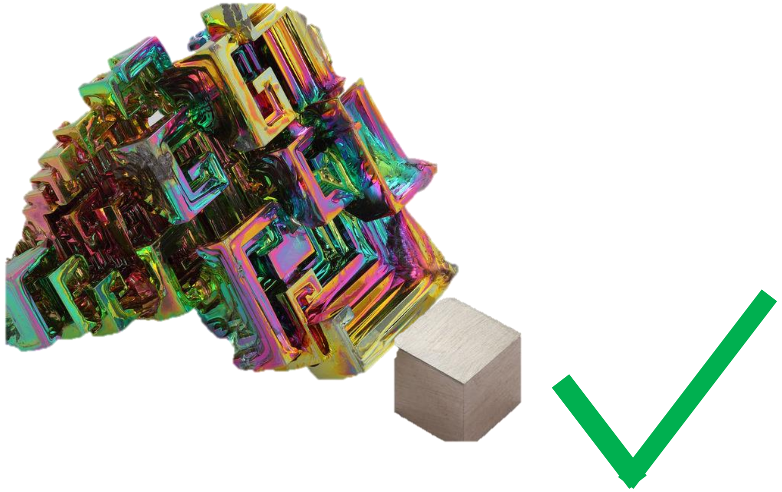
Experimental procedure →conventional method

<u>Compositions</u>

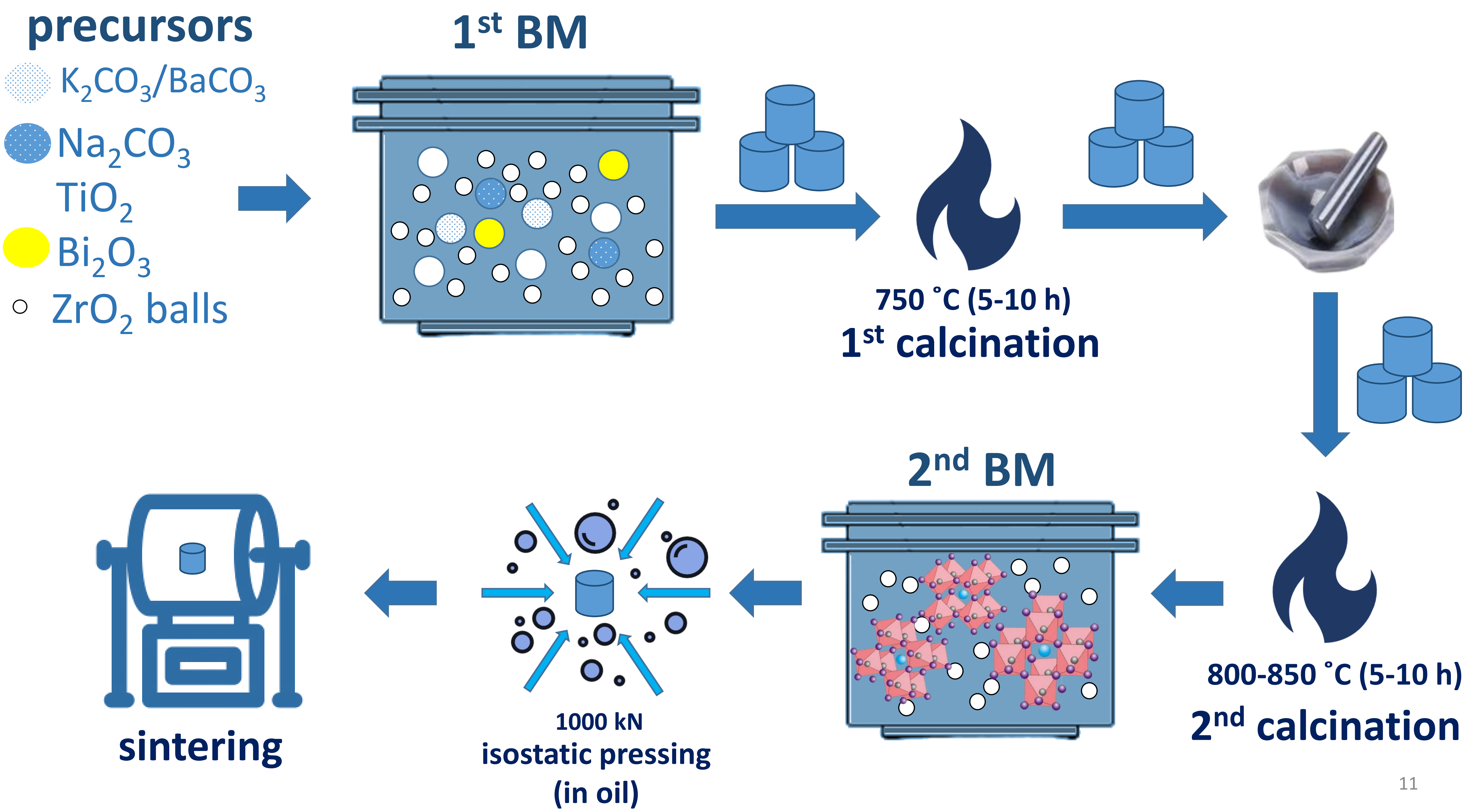
1) NBT-20KBT
2) NBT-8KBT-4BT
3) NBT-5KBT-5BT

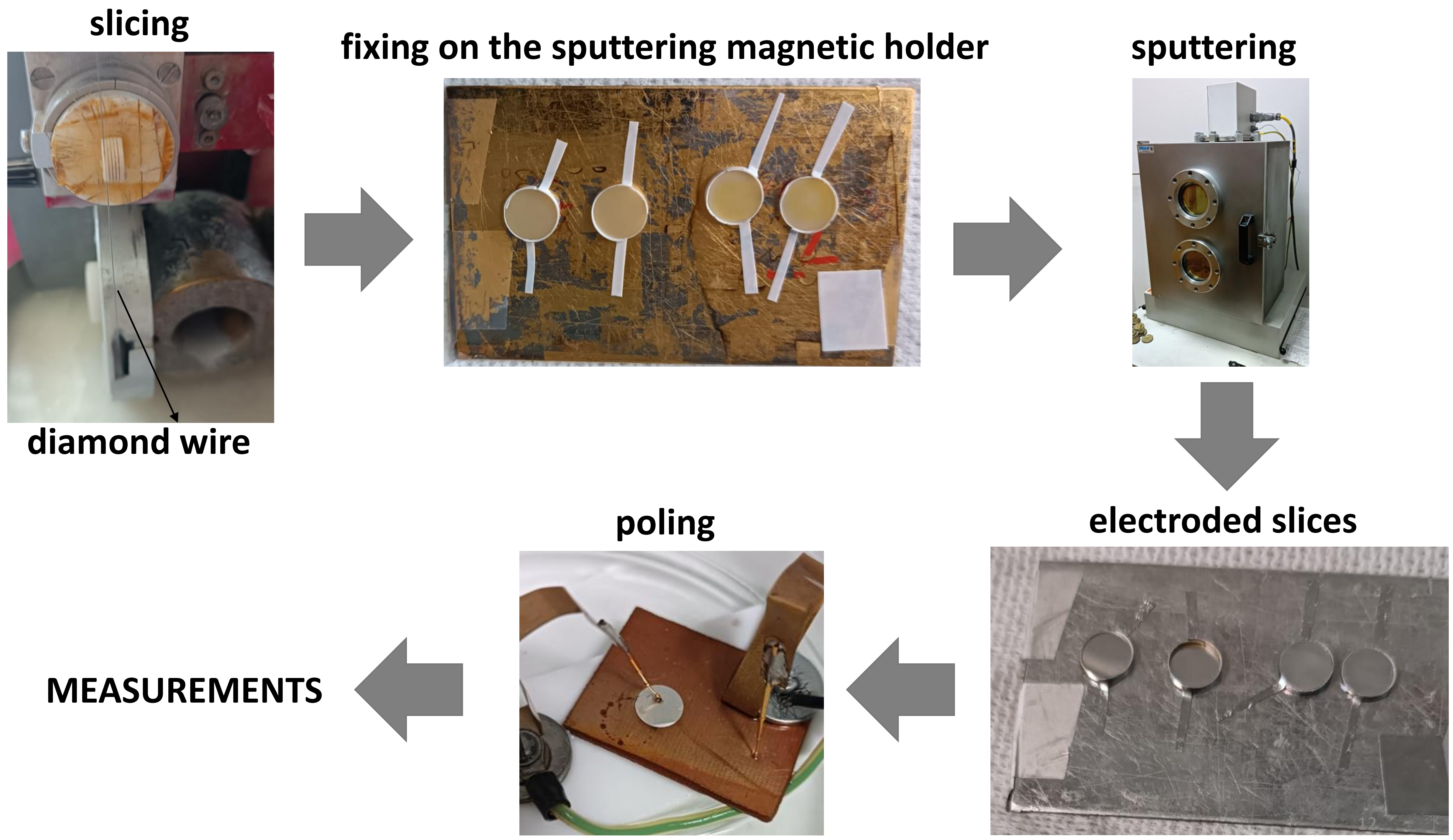
Why bismuth and not lead ?



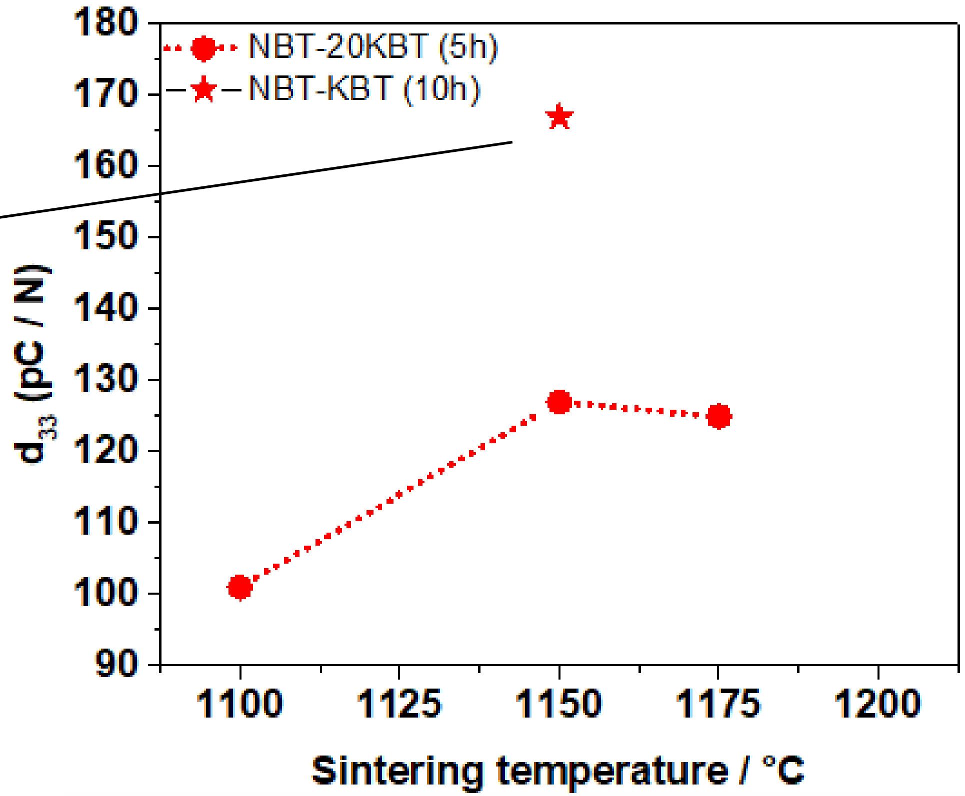


How the pellets and discs are made?

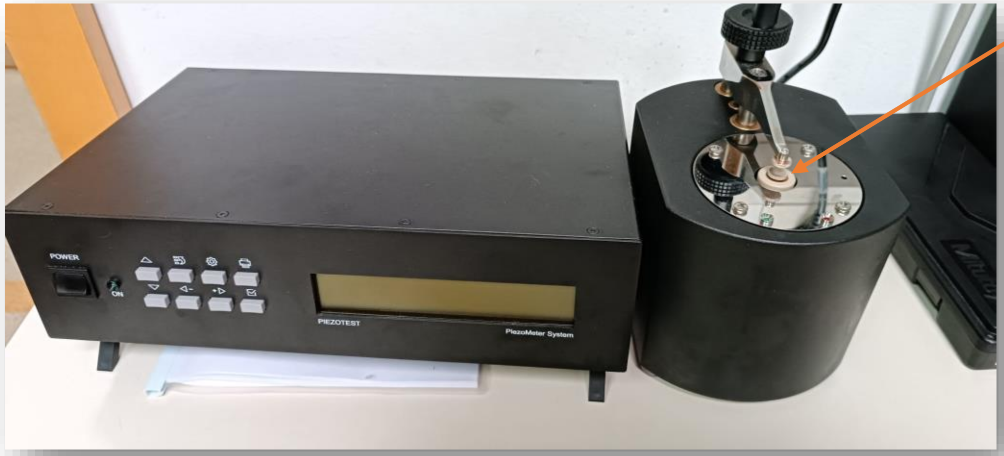

precursors
$K_2CO_3/BaCO_3$
Na_2CO_3
TiO_2
Bi_2O_3
ZrO_2 balls
1st BM
750 ˚C (5-10 h)
1st calcination
800-850 ˚C (5-10 h)
2nd calcination
2nd BM
1000 kN
isostatic pressing
(in oil)
sintering


slicing
diamond wire
fixing on the sputtering magnetic holder
sputtering
electroded slices
poling
MEASUREMENTS

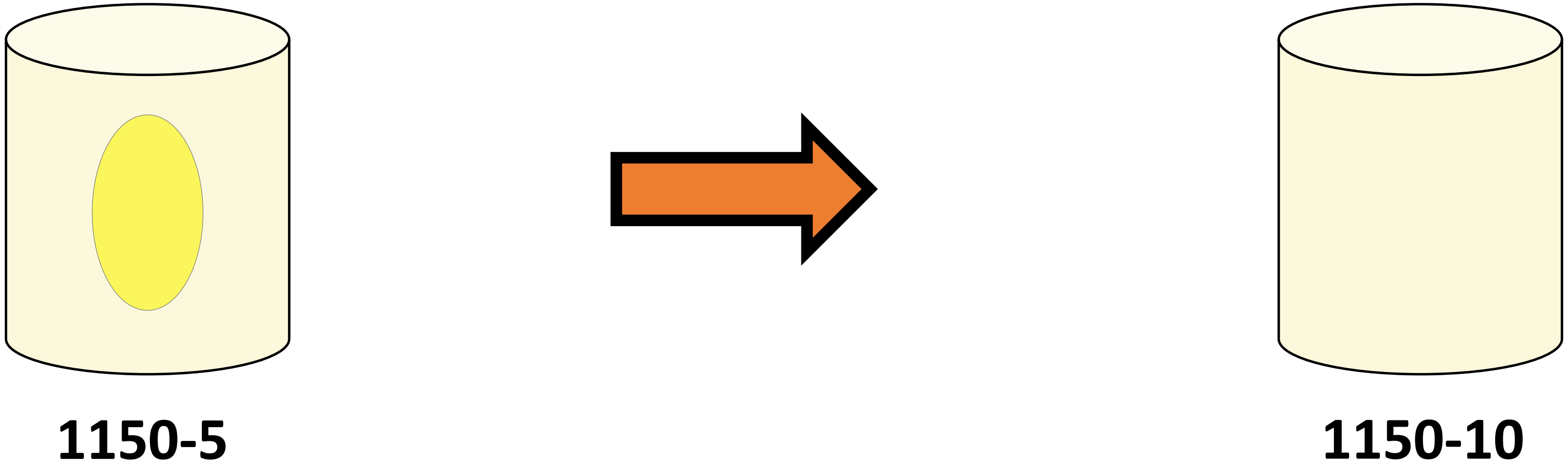
How to explain sudden increase in piezoelectric properties?



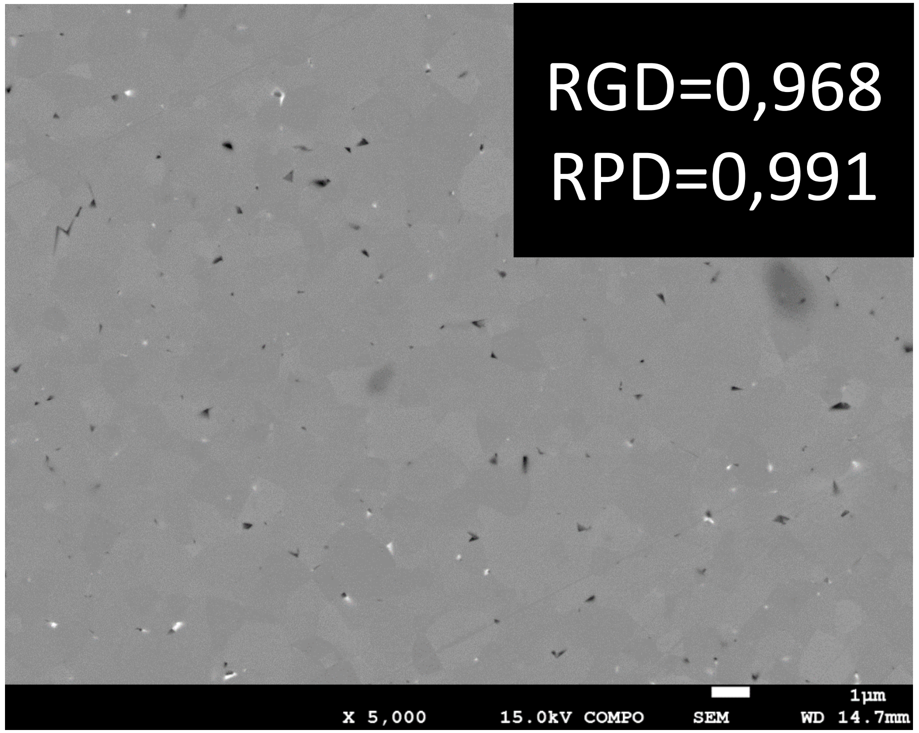
poled sample



Strange phenomena

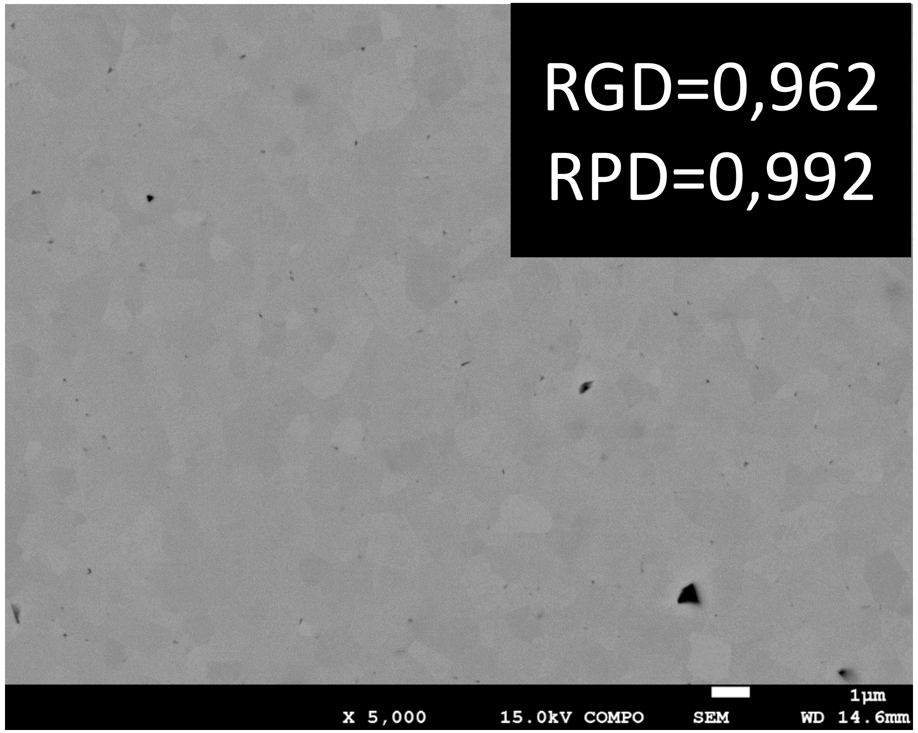


1150-5

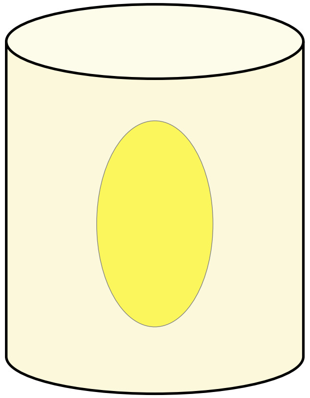


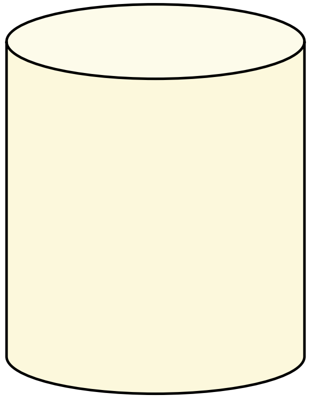
Secondary phases (Bi rich phase)

1150-10



No secondary phases





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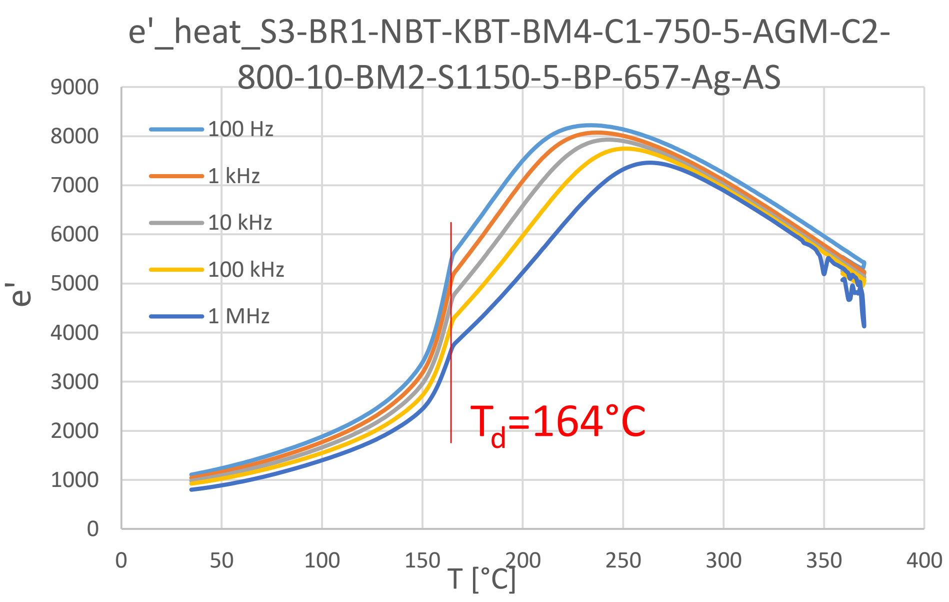

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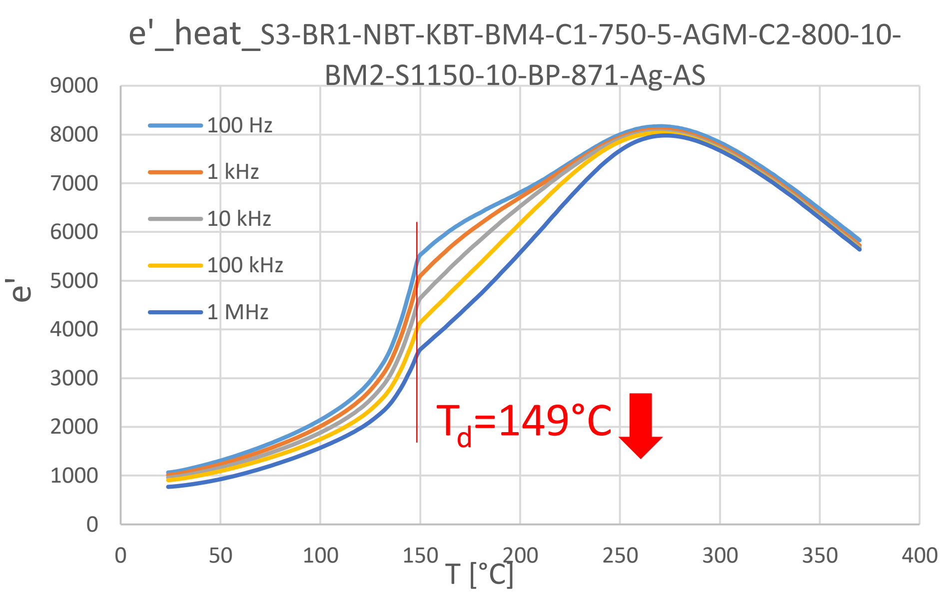
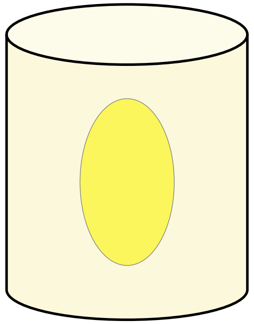
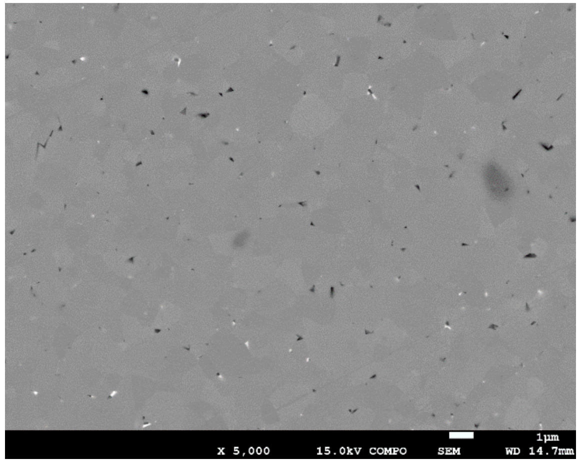


NBT-20KBT

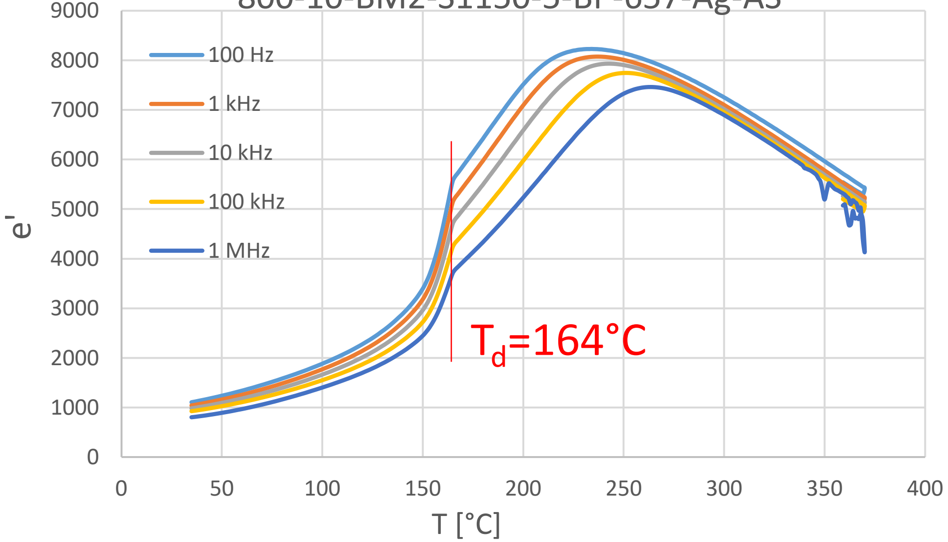
Is there a connection?

1150-5

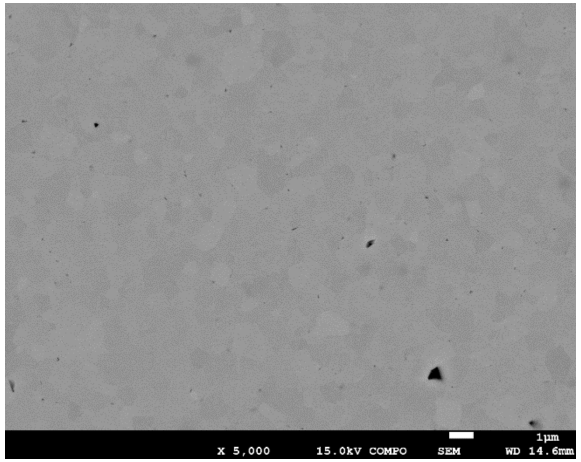


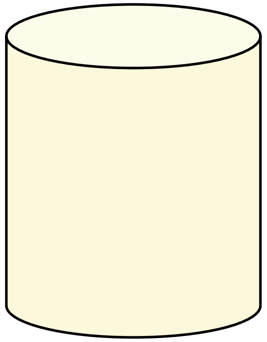


e'_heat_S3-BR1-NBT-KBT-BM4-C1-750-5-AGM-C2-800-10-BM2-S1150-5-BP-657-Ag-AS



1150-10





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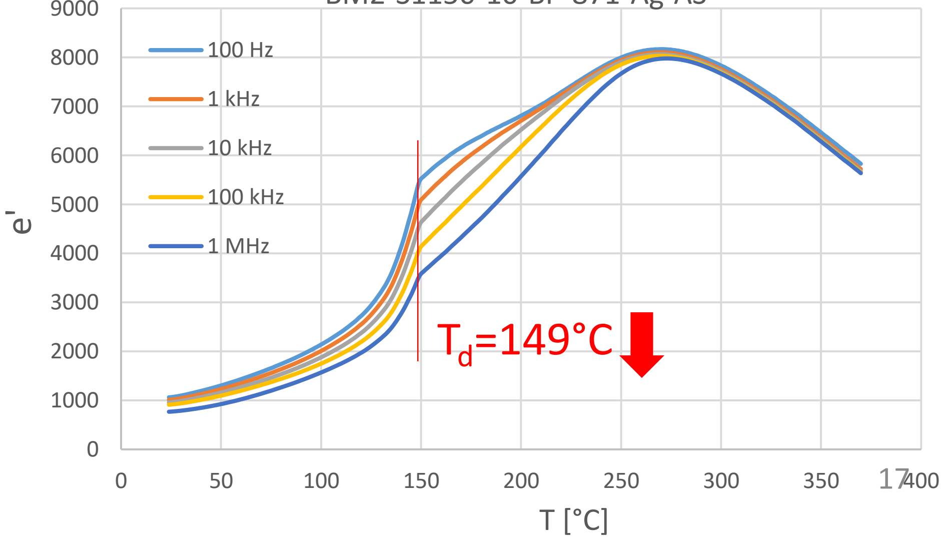
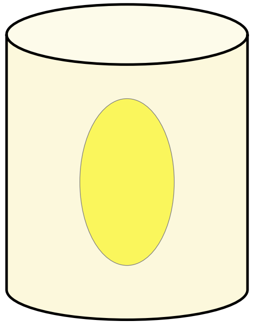
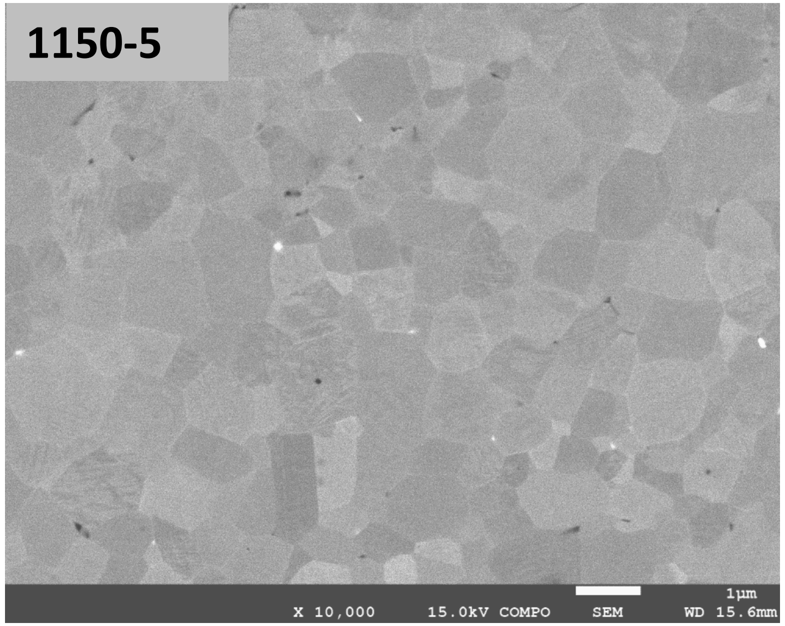
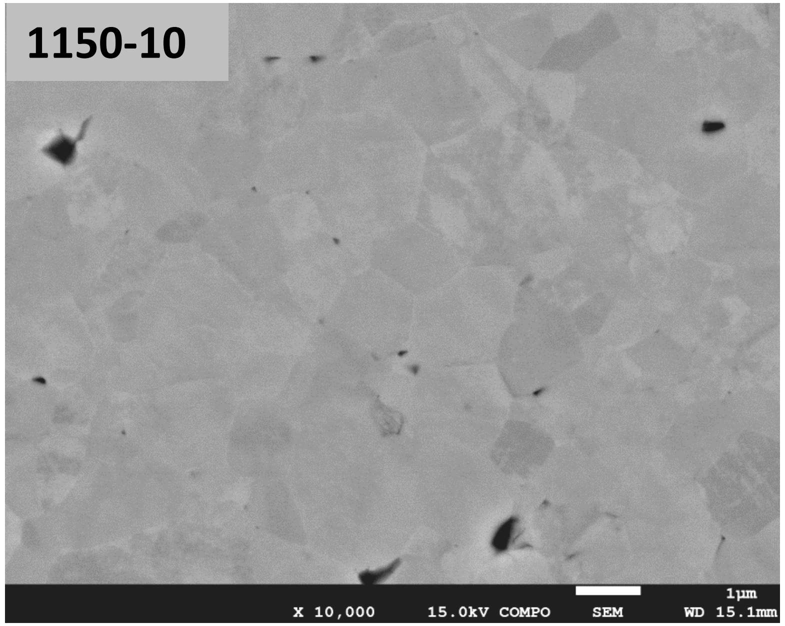
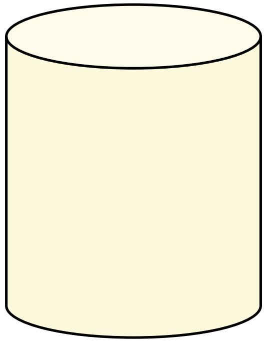


NBT-8KBT-4BT

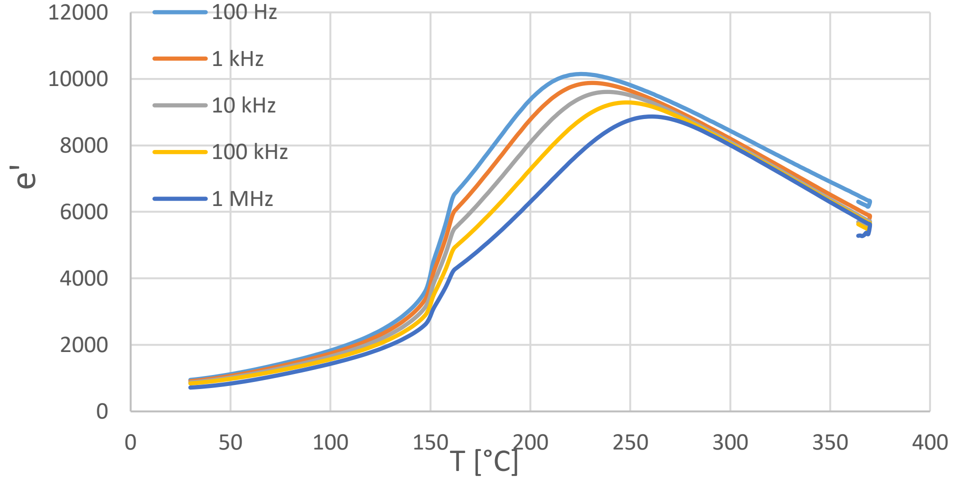








e'_heat_S1-BNT-8KBT-4BT-BM2-C1-750-10-AGM-C2-800-5-AGM-BM1-S1150-5-BP-838-20-Ag-AS-YC



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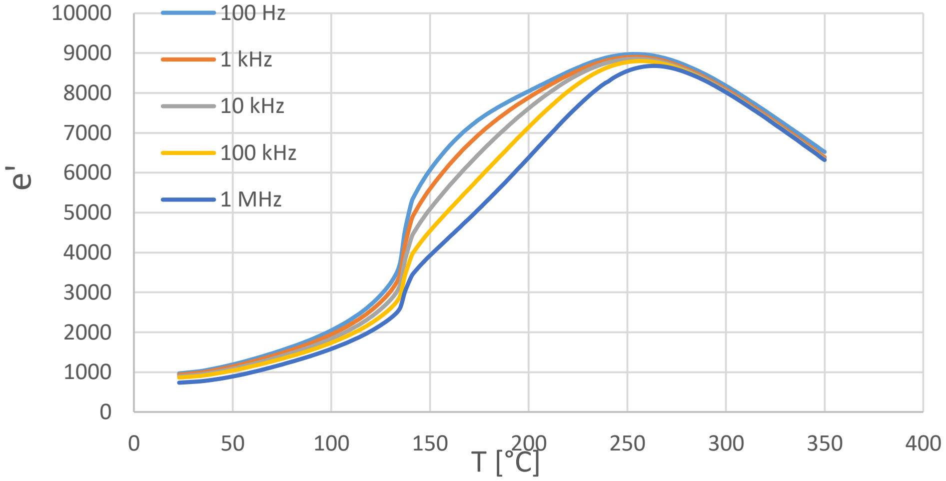
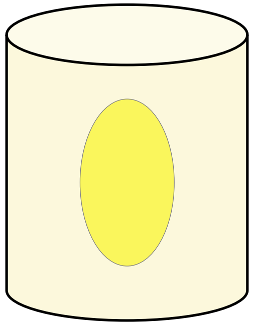
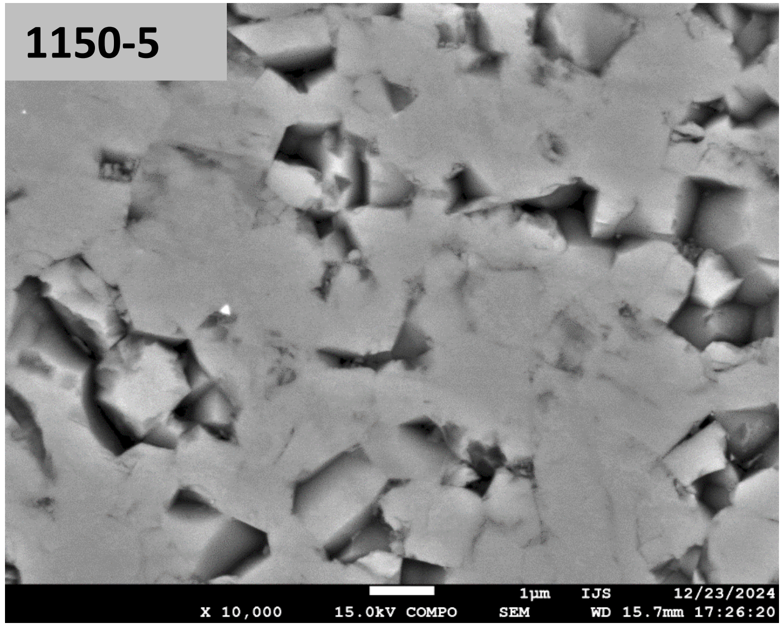
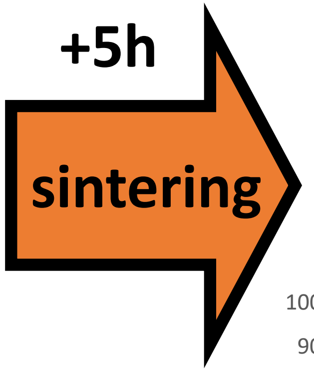
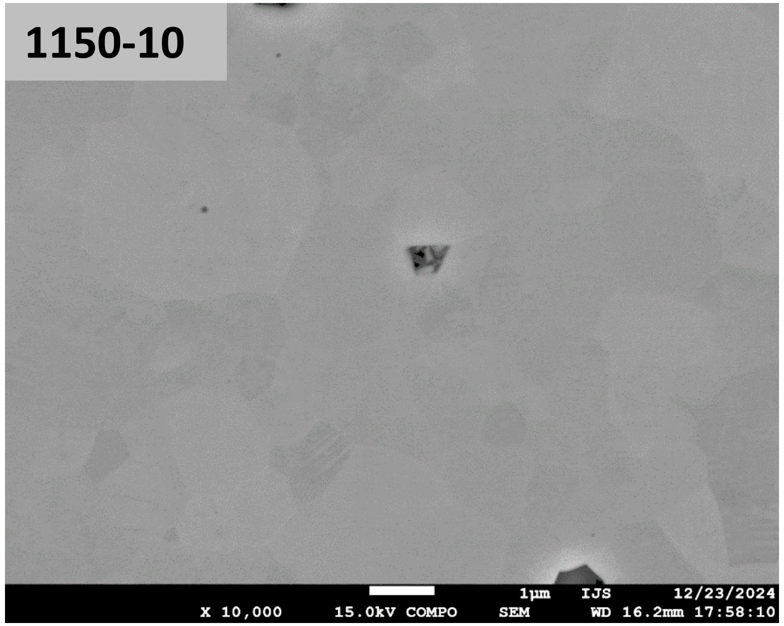


NBT-5KBT-5BT




1150-5
X 10,000 15.0kV COMPO SEM 1μm IJS WD 15.7mm 12/23/2024 17:26:20


+5h
sintering


1150-10
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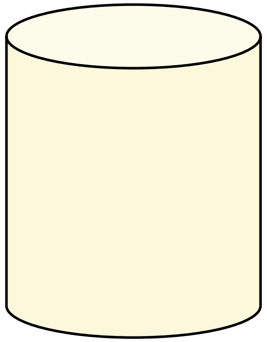
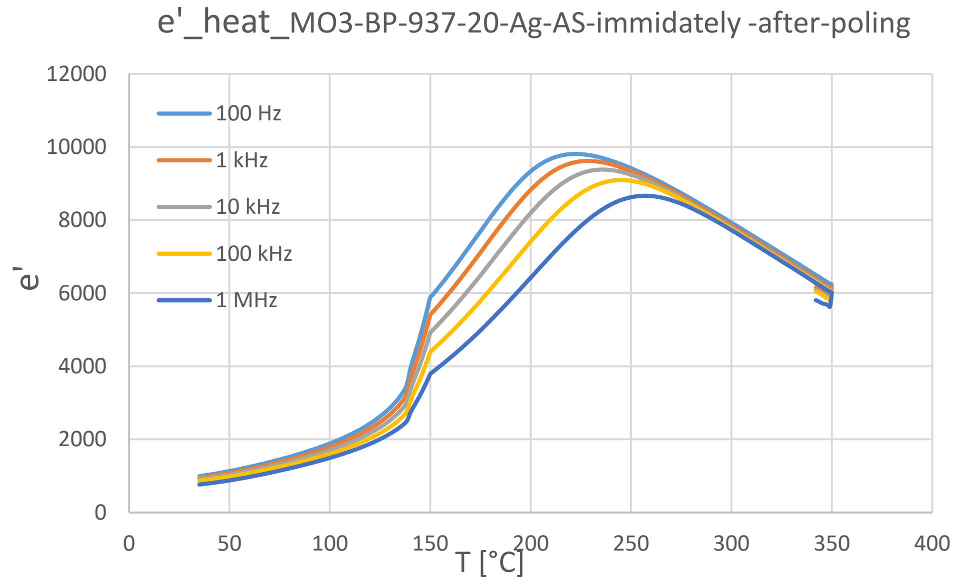
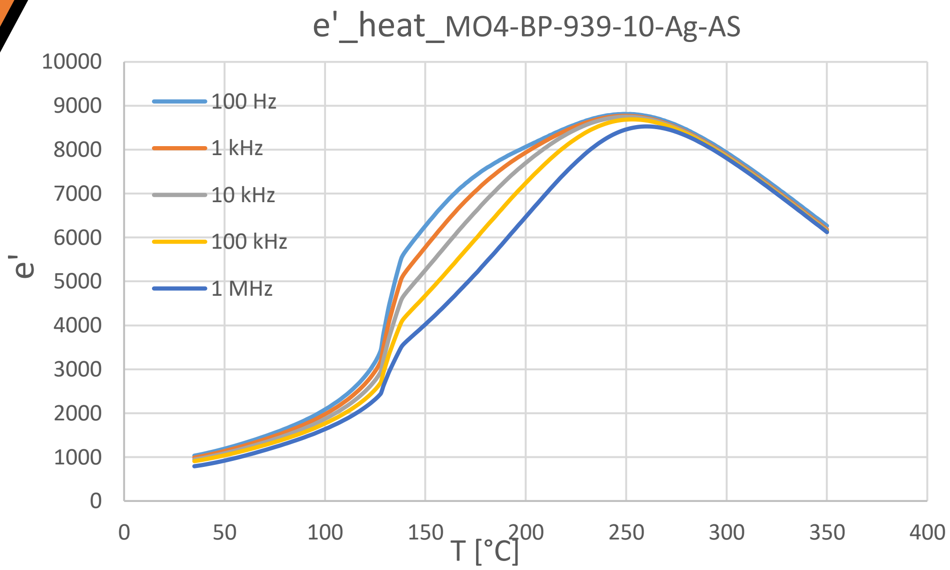



e'_heat_MO3-BP-937-20-Ag-AS-immidately -after-poling
e'
T [°C]
100 Hz
1 kHz
10 kHz
100 kHz
1 MHz
0
2000
4000
6000
8000
10000
12000
0 50 100 150 200 250 300 350 400


e'_heat_MO4-BP-939-10-Ag-AS
e'
T [°C]
100 Hz
1 kHz
10 kHz
100 kHz
1 MHz
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
0 50 100 150 200 250 300 350 400

Questions to be answered

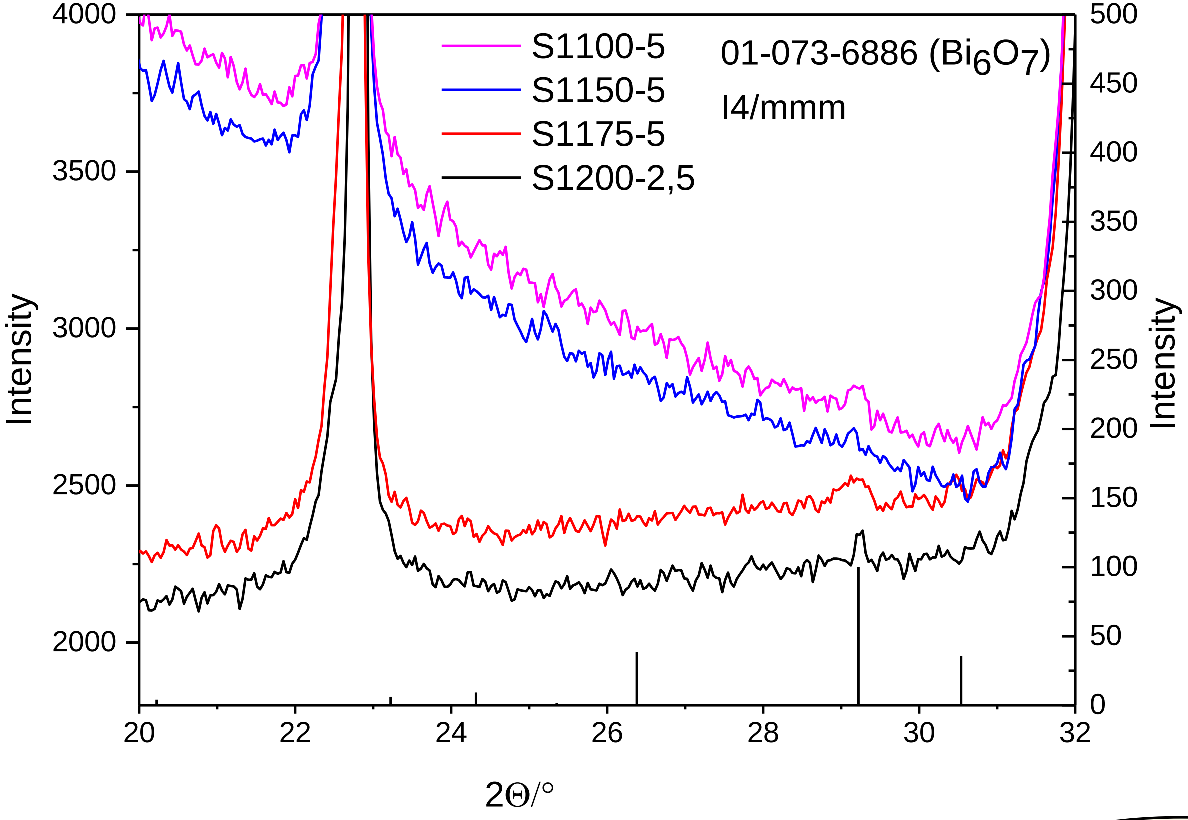
- Secondary phase ad triple junctions between grains in the microstructure
  - →Secondary phases and connection with yellow patterns?
  - →Do we have solid state sintering or transient liquid phase sintering?
- Why is frequency dispersion lost upon 5h prolonged sintering at 1150 °C ?

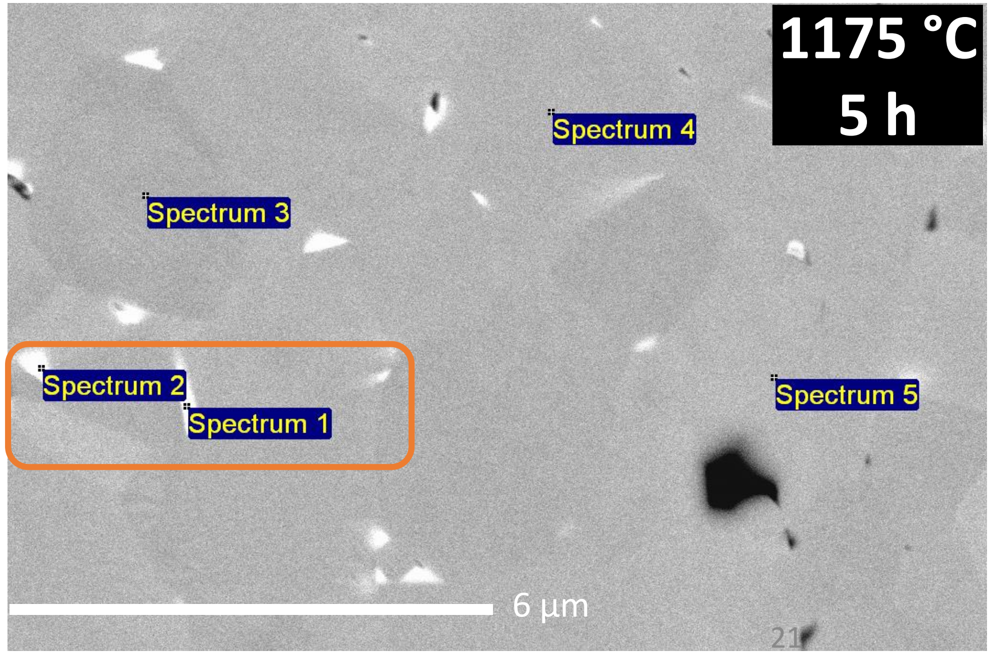
NBT-KBT

Secondary phases

Bi rich phase

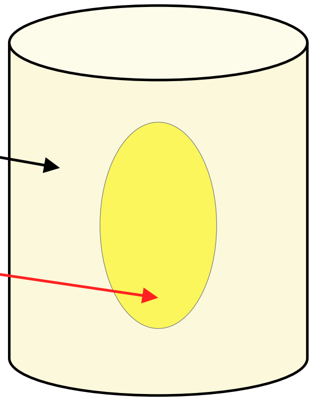
Spectrum	Na / At. %	K/ At. %	Ti/ At. %	Bi/ At. %	O/ At. %
Spectrum 1	8.22	0.00	17.61	13.28	60.23
Spectrum 2	8.62	0.24	16.88	13.76	59.83
Spectrum 3	8.14	0.00	20.79	10.16	60.90
Spectrum 4	7.77	0.00	21.01	10.12	61.09
Spectrum 5	8.62	0.00	20.92	9.72	60.74





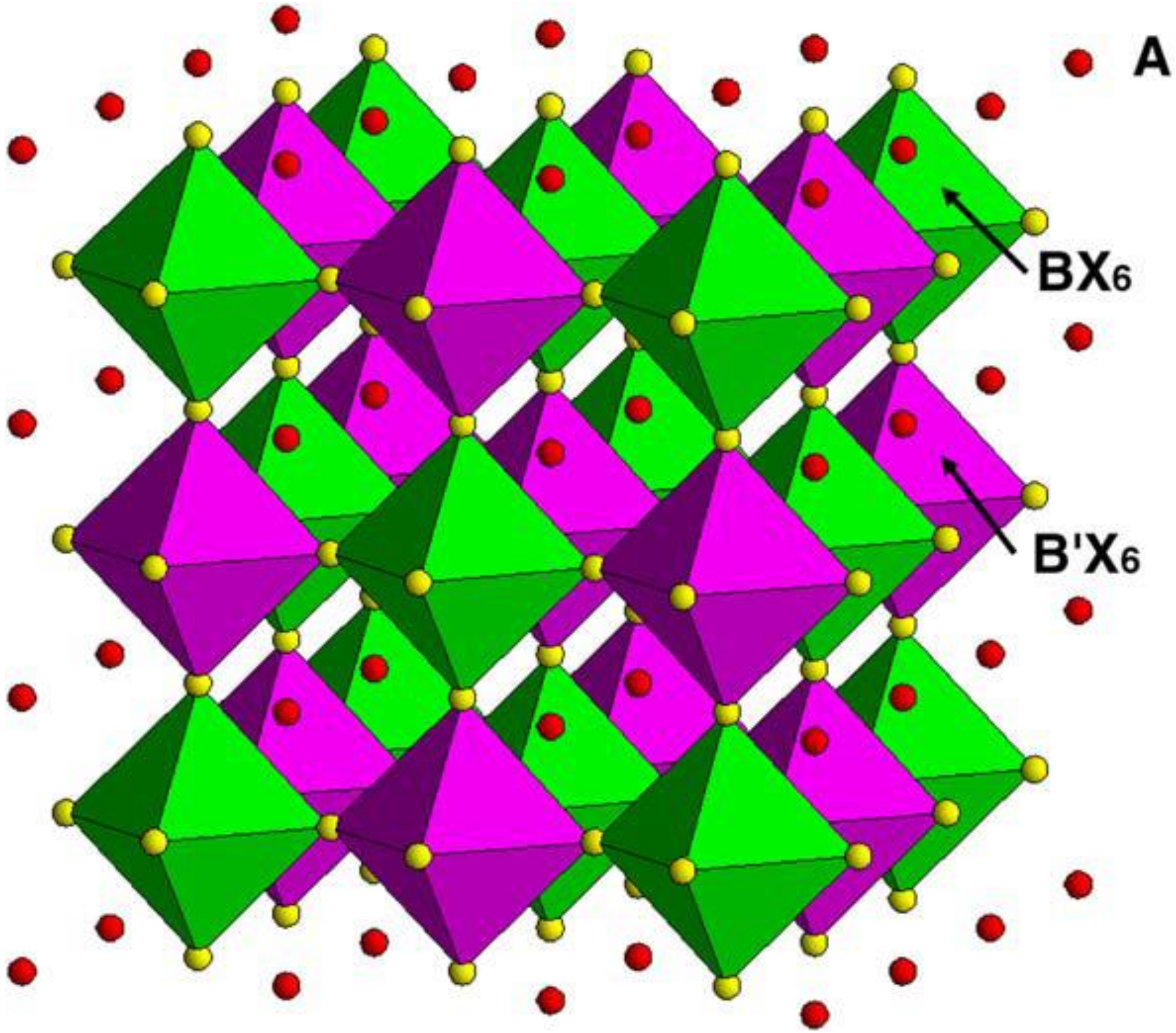
Literature:
$Bi_4Ti_3O_{12}$
$Bi_2Ti_2O_7$

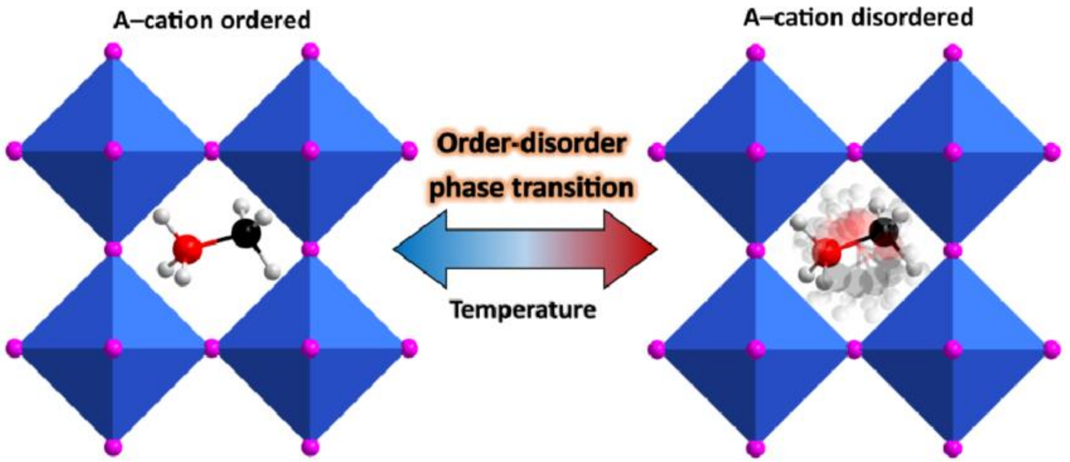
Solid state sintering
+
Local liquid phase sintering



Hou et al. **J. Am. Ceram. Soc.** 100 (2017) 1330-1338
Emilio Pradal-Velazquez et al. **J. Am. Ceram. Soc.** 103 (2020) 6801-6810
Roberto Esquivel-Elizondo et al. **Chem. Mater.** 23 (2011) 4965-4974

Example of B site ordering





A-site disordering → A-site 1:4 ordering

1150 °C-10 h

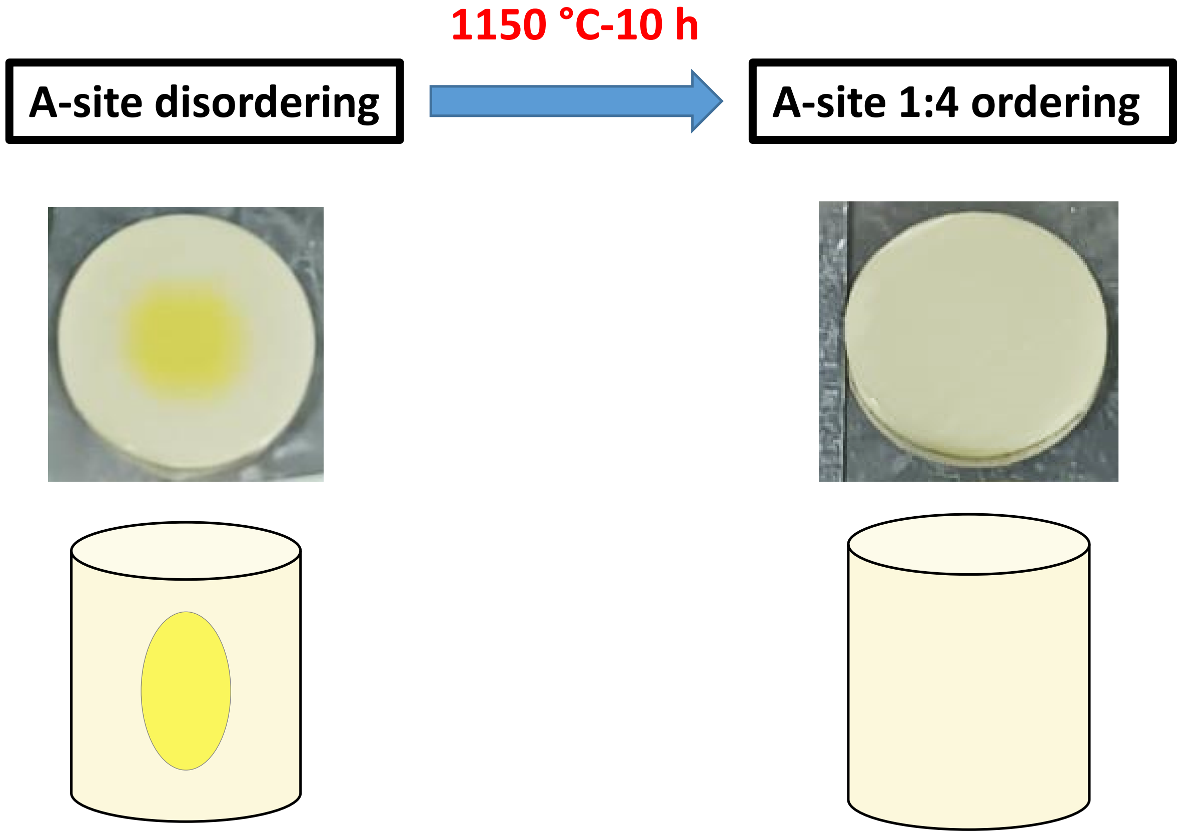
King et al. **J. Mater. Chem.** 20 (2010) 5785-5796

Mitchell et al. **Mineral. Mag.** 81 (2017) 411-461

Stenger et al. **phys. stat. sol. 61** (1980) 275

Conclusion

- All three different NBT compositions compositions gave the same phenomena
- Yellow color is probably due to bismuth rich secondary phase melted, causing the accumulation in the triple joints between grains
- Pellet inhomogeniety is resolved with prolonged sintering time, giving enhanced properties as a result
- A-site ordering appears, causing loss of frequency dispersion in permitivitty measurement



Special thanks to K5 members…

Odsek za
elektronsko keramiko K5

- Mojca Otoničar
- Andraž Bradeško
- Meryem Lachhab

- Nejc Špenko
- Lea Lončarić
- David Verdel

- Lia Šibav
- Silvo Drnovšek
- Brigita Kmet
- Andrej Debevec

Special thanks to ZKM

IRB research group

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Svetozar Musić

Stjepko Krehula

Marijan Marciuš

Željka Petrović

Nina Popov

Marko Dunatov

Mia Mesić

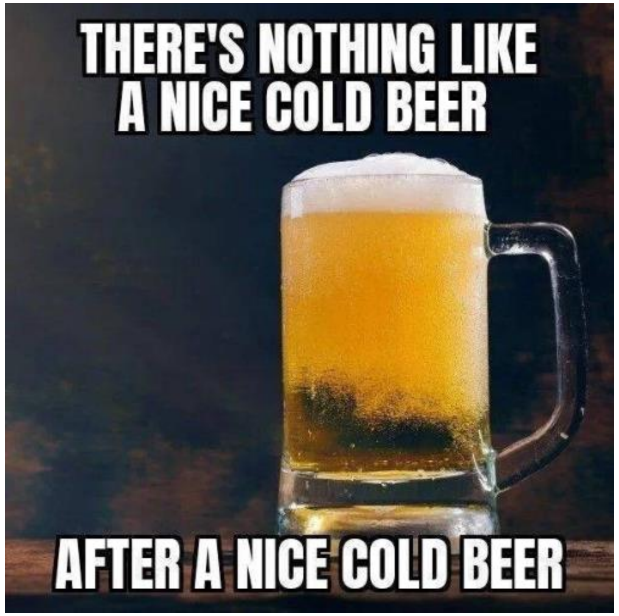
Glorija Medak

Ivana Landripet

Matej Bubaš

Nikol Bebić

Karlsruheri



Lidija-Androš Dubraja

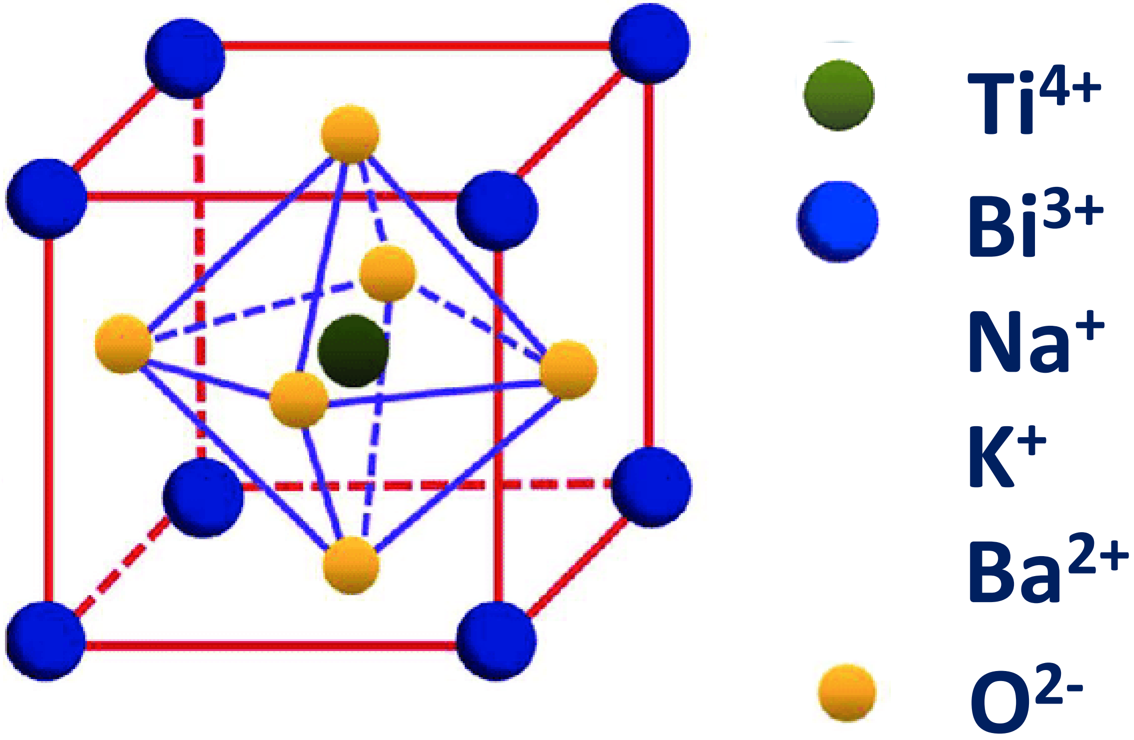
Andreas Puškarić

Marko Dunatov


THANK
YOU
FOR
YOUR
ATTENTION

Perovskite structure

ABO_3



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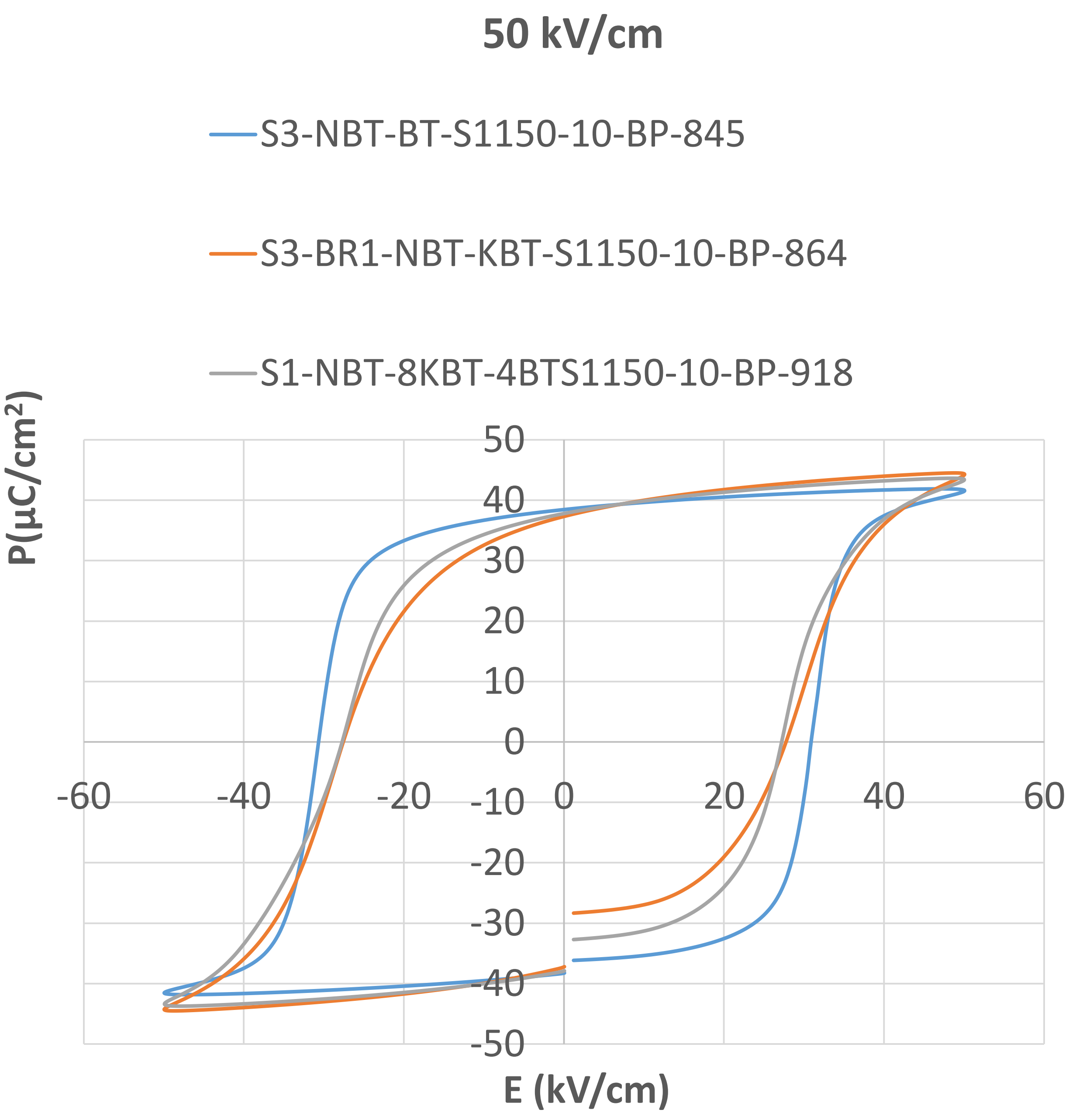
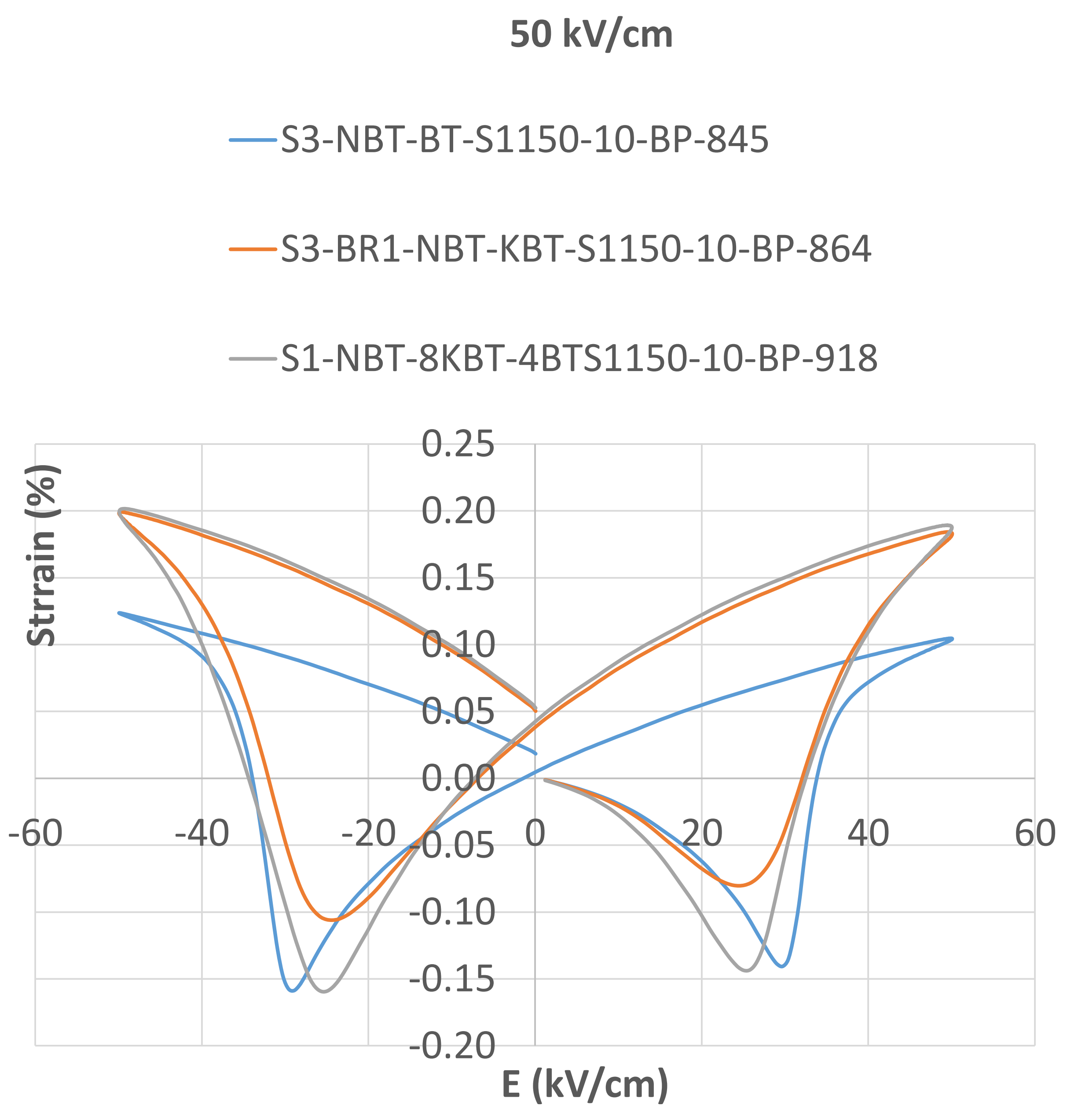
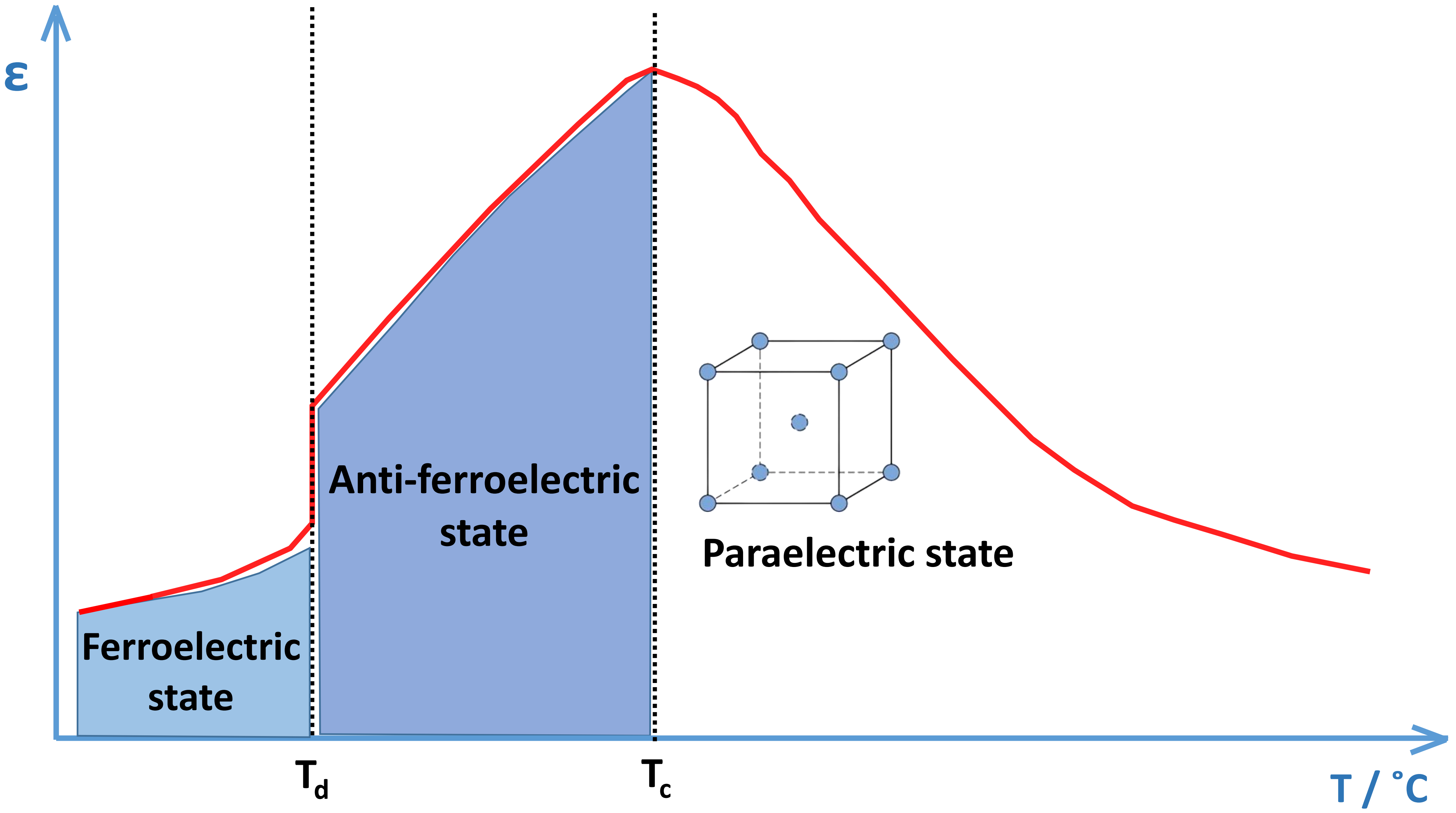
NBT-5KBT-5BT $0{,}90((Na_{0.5}Bi_{0.5})TiO_3)$ $0{,}05(K_{0.5}Bi_{0.5}TiO_3)$ $0{,}05$ $(BaTiO_3)$

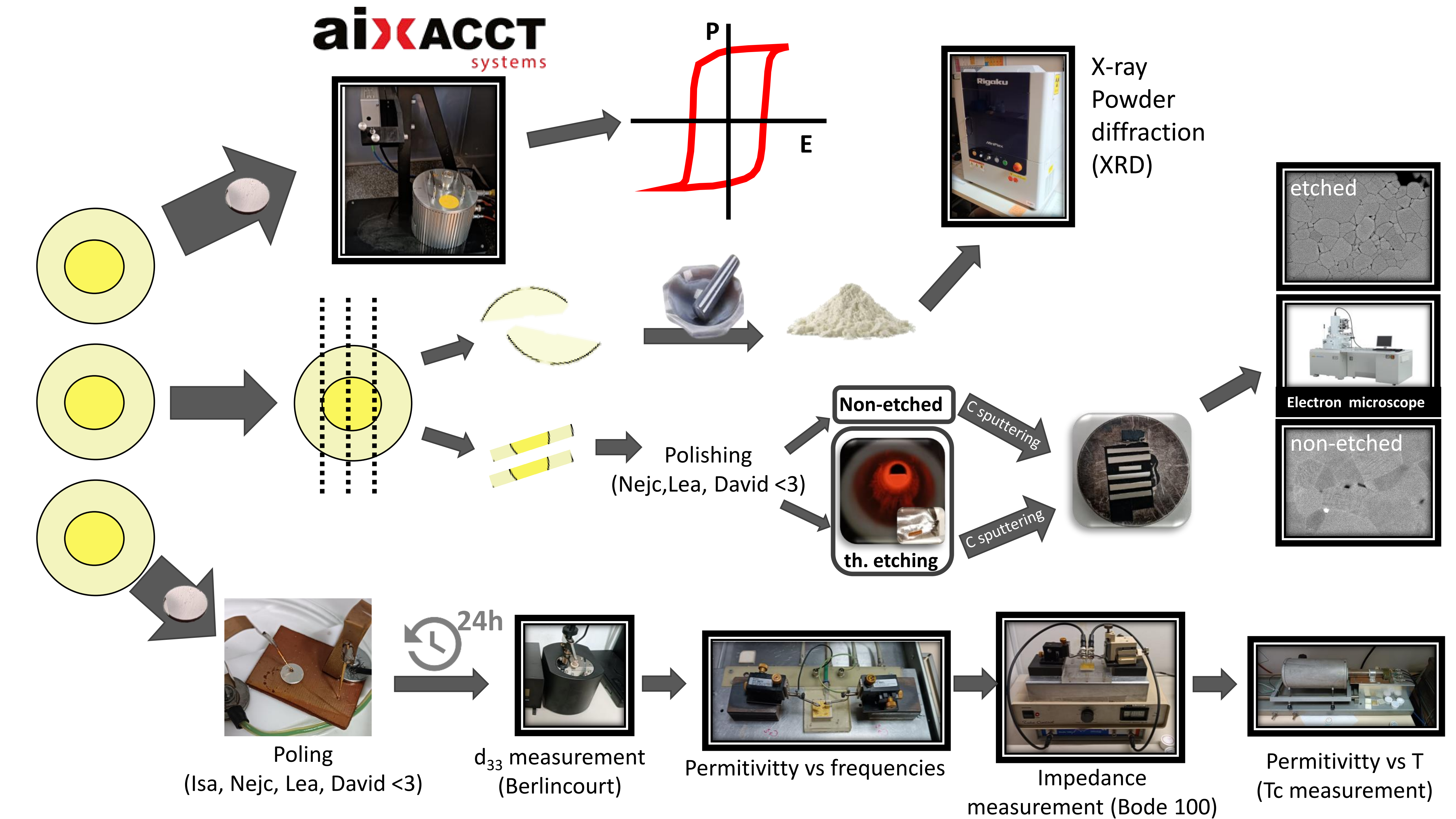
NBT-8KBT-4BT $0{,}88((Na_{0.5}Bi_{0.5})TiO_3)$ $0{,}08(K_{0.5}Bi_{0.5}TiO_3)$ $0{,}04$ $(BaTiO_3)$


50 kV/cm
S3-NBT-BT-S1150-10-BP-845
S3-BR1-NBT-KBT-S1150-10-BP-864
S1-NBT-8KBT-4BTS1150-10-BP-918
P(µC/cm²)
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-40
-20
0
20
40
60
E (kV/cm)

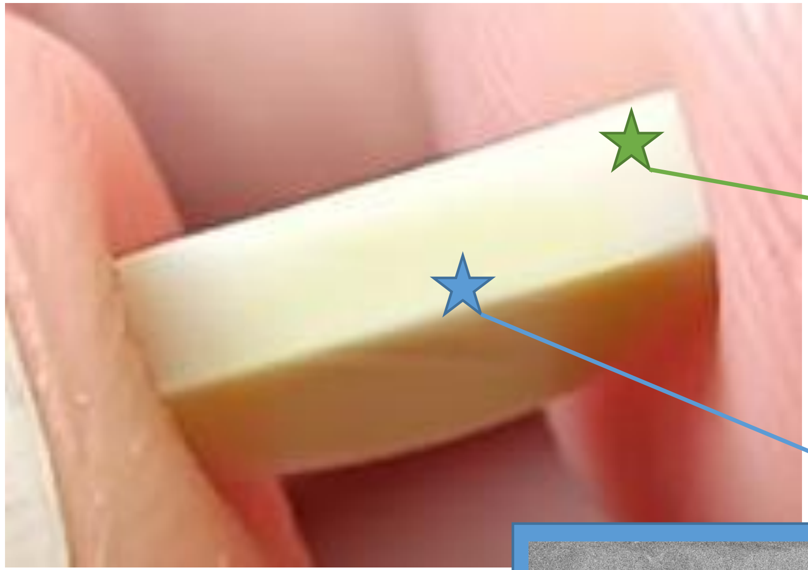

50 kV/cm
S3-NBT-BT-S1150-10-BP-845
S3-BR1-NBT-KBT-S1150-10-BP-864
S1-NBT-8KBT-4BTS1150-10-BP-918
Strain (%)
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
-0.10
-0.15
-0.20
-60
-40
-20
0
20
40
60
E (kV/cm)

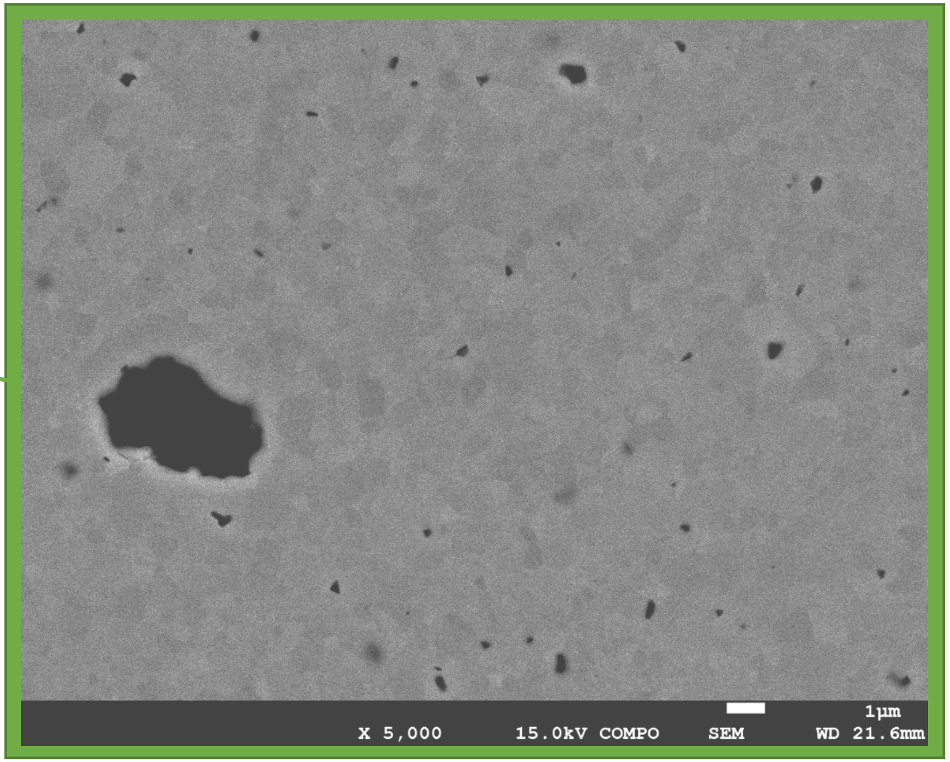
T_c measurement after poling

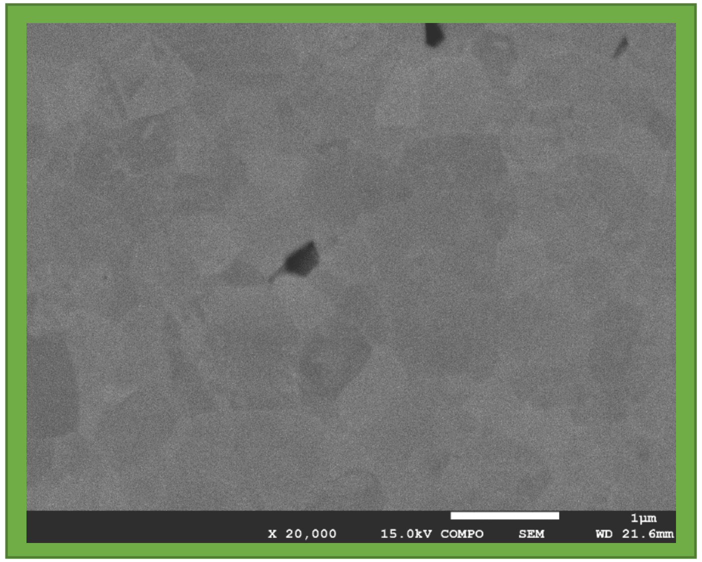


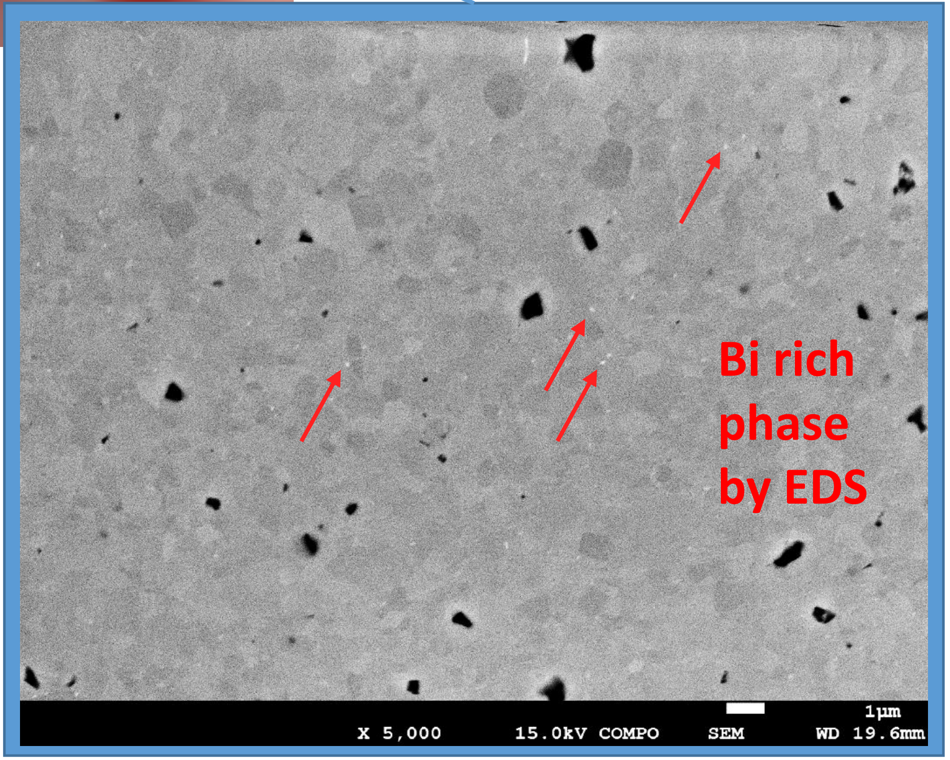

aixACCT
systems
P
E
X-ray
Powder
diffraction
(XRD)
etched
Electron microscope
non-etched
Non-etched
C sputtering
th. etching
C sputtering
Polishing
(Nejc,Lea, David <3)
24h
Poling
(Isa, Nejc, Lea, David <3)
d_{33} measurement
(Berlincourt)
Permitivitty vs frequencies
Impedance
measurement (Bode 100)
Permitivitty vs T
(Tc measurement)

S1-NBT-8KBT-4BT-BM2-C1-750-10-AGM-C2-800-5-AGM-BM1-S1100-5-top slice

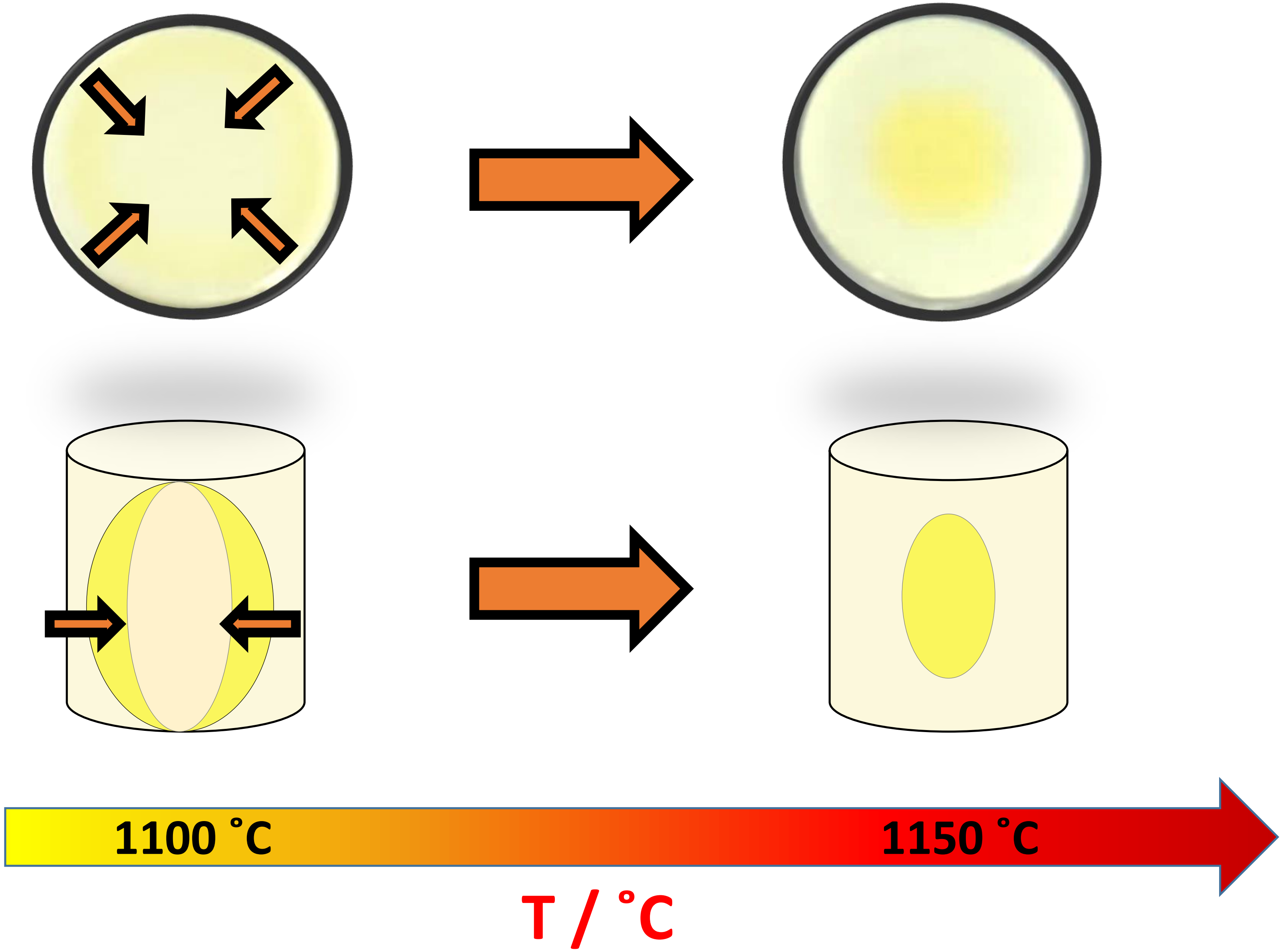




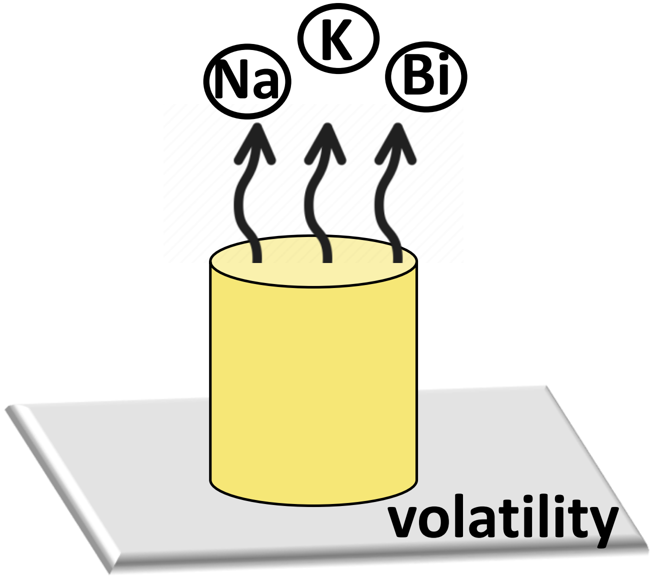




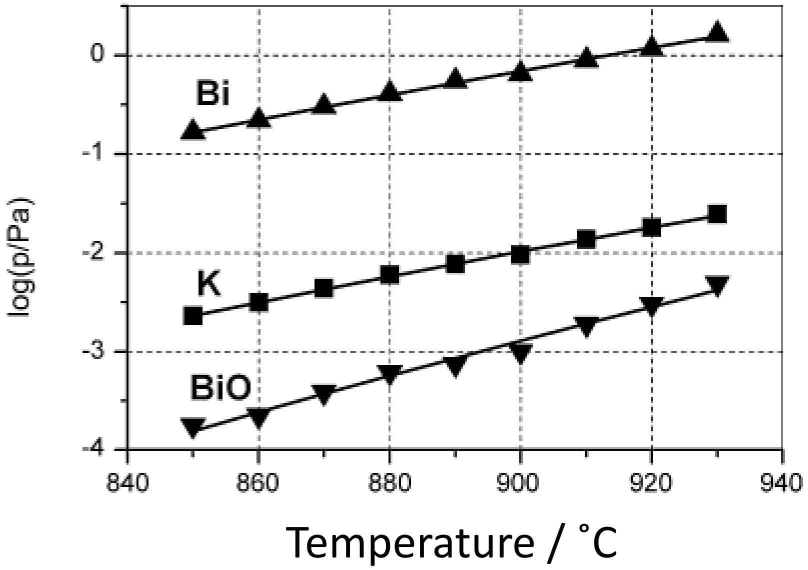
5h sintering

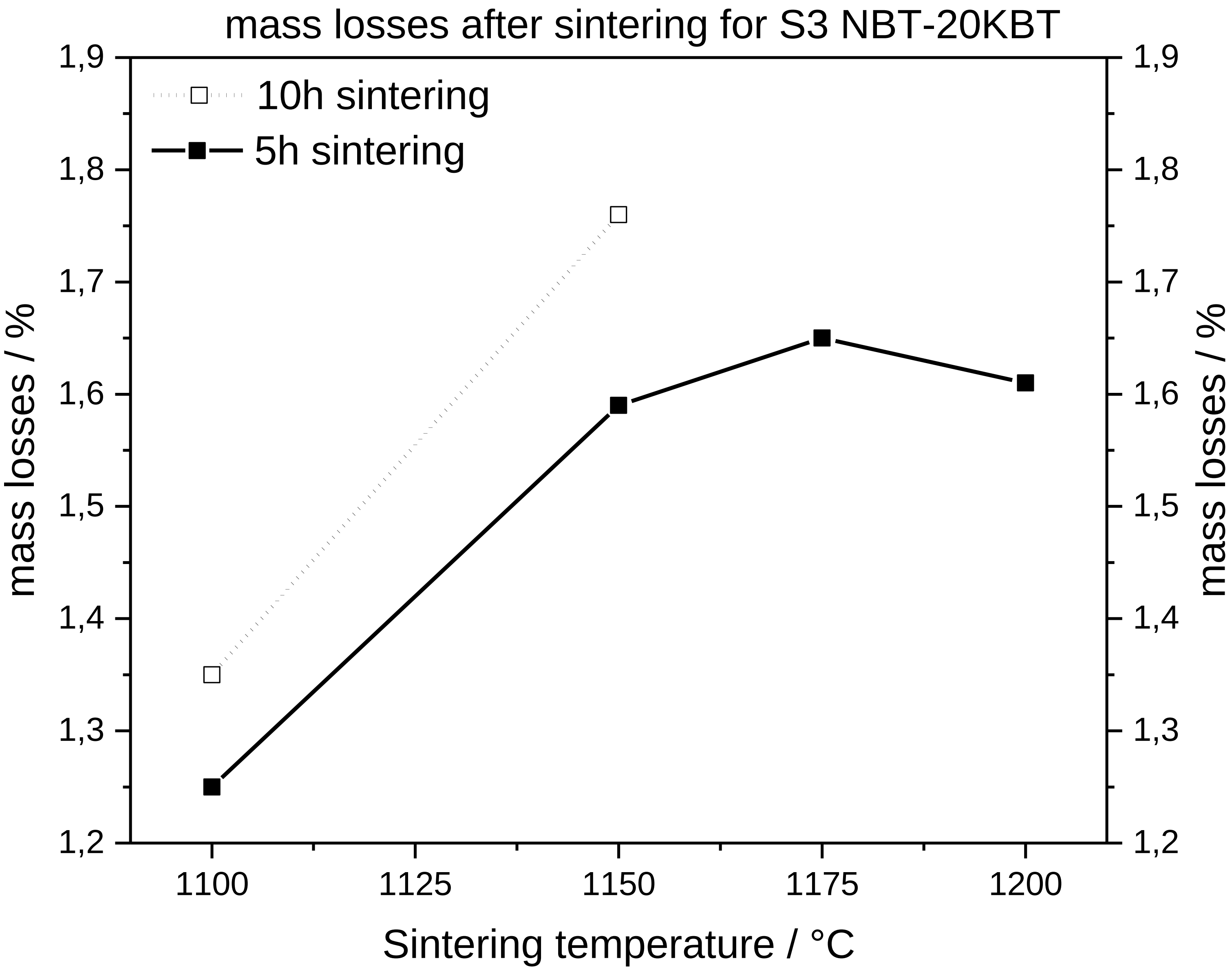


Mass losses



Knudsen cell
Calcined KBT-vapour pressure





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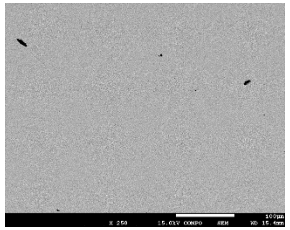
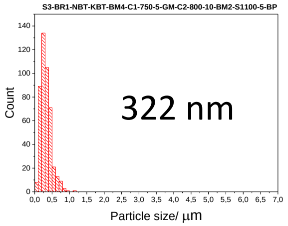
NBT-20KBT

S1100-5

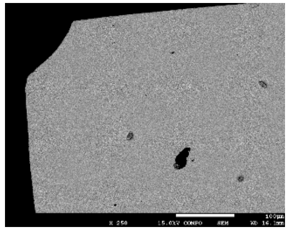


RGD=0,948
RPD=0,997



101 pC/N

S1100-10



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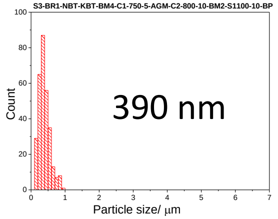
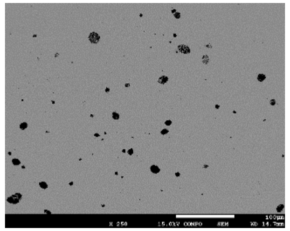
RPD=0,990

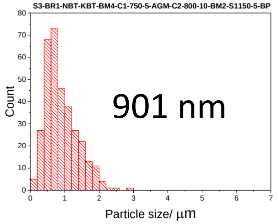


burned

S1150-5

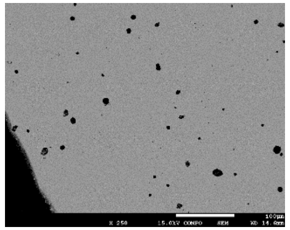


RGD=0,968
RPD=0,991



127 pC/N

S1150-10



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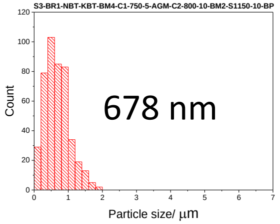
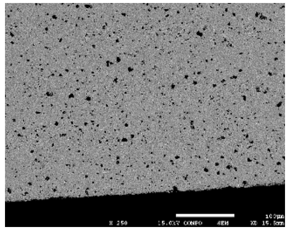
RPD=0,992



167 pC/N

1175-5



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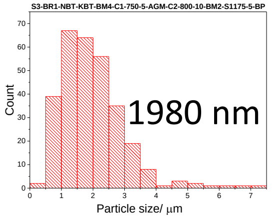
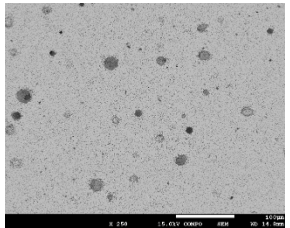
RPD=0,982

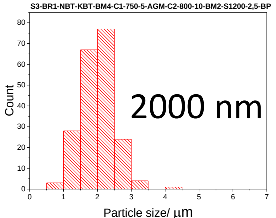


125 pC/N

1200-2,5



RGD=0,885
RPD=0,978



Could not be poled