Towards process simplification for shaping and sintering of KNN piezoelectric perovskite powders: SPS route for screen-printed thick films

H. Debéda[1], B. Plano[1],
U.C. Chung[2], M. Maglione[2], C. Elissalde[2]

[1]Université de Bordeaux, Laboratoire IMS, Talence, France

[2]Laboratoire ICMCB, CNRS, Pessac, France

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Outline

Towards process simplification for shaping and sintering of KNN piezoelectric perovskite powders: SPS route for screen-printed thick films

1. **Context and objectives**

2. **Previous results on $PbZrTiO_3$ (PZT) piezo ceramics**

3. **Towards $(K,Na)NbO_3$ (KNN) piezo ceramics**

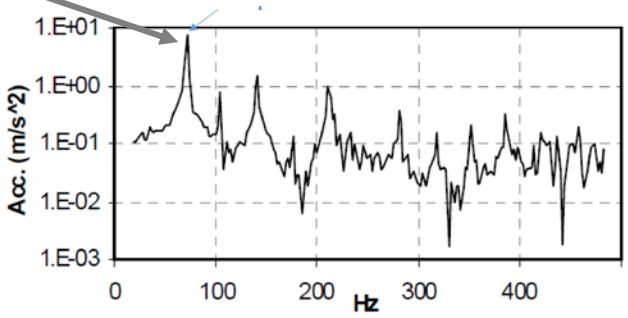
4. **Conclusion**

Context

ENVIRONMENT ENERGY HARVESTING

Thermal | **Vibrations** | Radiation | Biological

Vibration source	Acceleration ($m\ s^{-2}$)	$Frequency_{peak}$ (Hz)
Car engine compartment	12	200
Base of 3-axis machine tool	10	70
Blender casing	6.4	121
Clothes dryer	3.5	121
Person tapping their heel	3	1
Car instrument panel	3	13
Door frame just after door closes	3	125
Small microwave oven	2.5	121
HVAC vents in office building	0.2–1.5	60
Windows next to a busy road	0.7	100
CD on notebook computer	0.6	75
Second story floor of busy office	0.2	100



Widely available

- Important data are frequency, acceleration or force
- Wide power range (*10* µW - *1* W)

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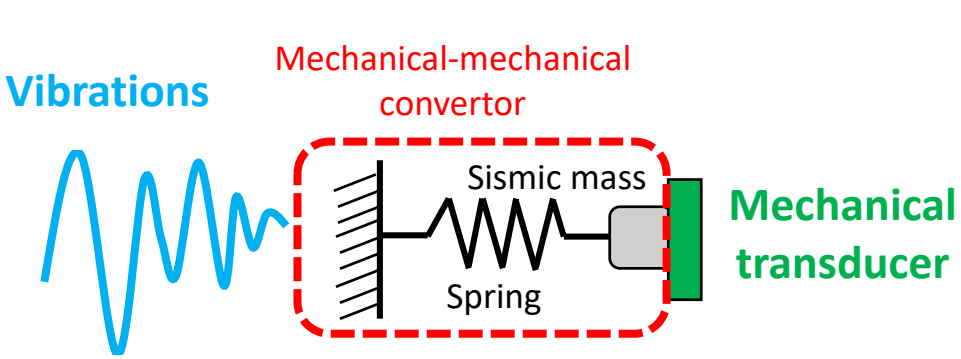
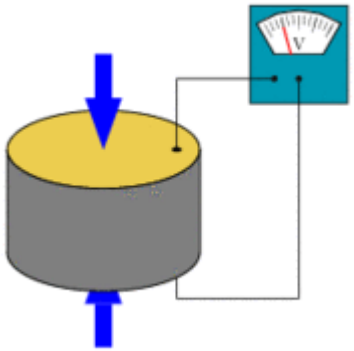
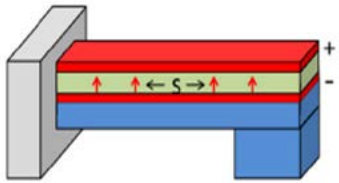
Context

ENVIRONMENT VIBRATION ENERGY HARVESTING







Piezoelectric unimorph in 31-mode

Piezoelectric MEMS Vibration EH

$$V_{oc} = \frac{d_{31}}{\varepsilon_r \varepsilon_0} \sigma_{31} t$$

σ_{31}: Mechanical stress (*Pa*)
t : Distance between electrodes (*m*)
ε_r: Relative dielectric constant
ε_0: Permittivity of vacuum ($F.m^{-1}$)
d_{31}: Piezoelectric coefficient (CN^{-1}).

Smart Mater. Struct. **28** (2019) 113001

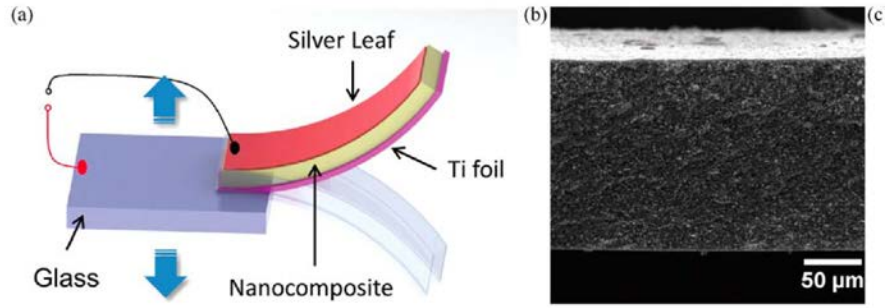
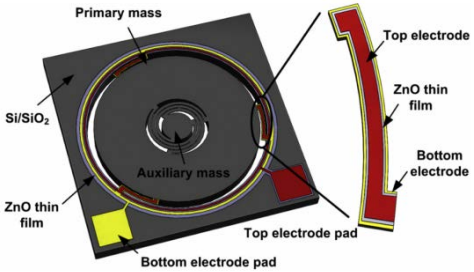


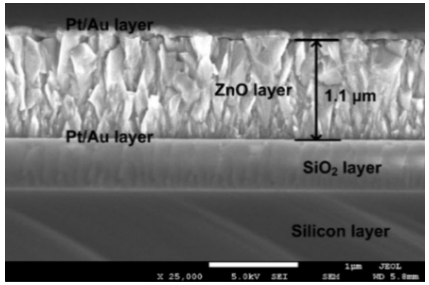
Figure 1. (a) Schematic diagram of the BZT–BCT NW/PDMS energy harvester; (b) and (c) cross-s

Objectives

Piezoelectric MEMS Vibration EH

ZnO thin films
Sputtered on Si

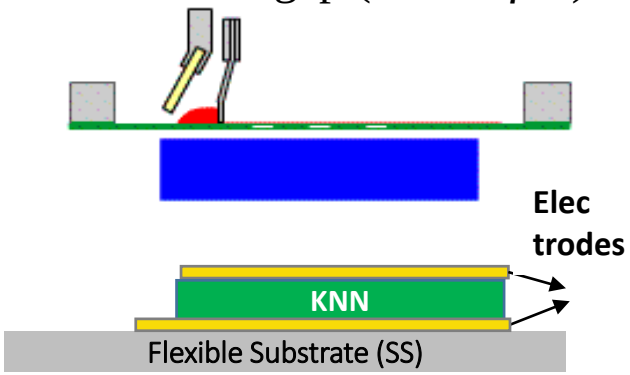




(Tao K. et *al*. 2019)

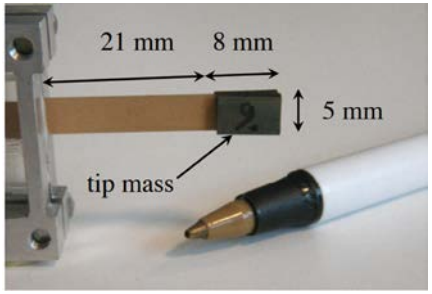
0.46 nW

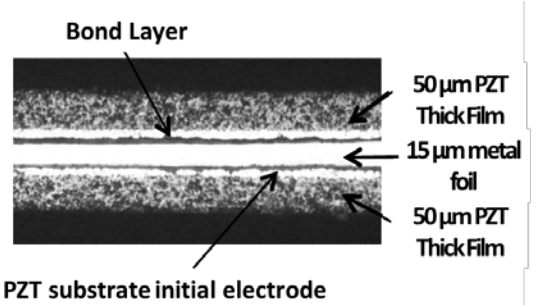
Thick film technology to fill fabrication gap (10-100µm)



- **Inorganic piezo + flexible** substrate
- Reduce process **cost**
- Harvested power (Tens of µW),
- Vibration frequency < 200Hz
- Reliability piezo. MEMS VEH.

Thinned PZT ceramic
Bonded on a SS substrate





(Colin et *al*. 2013)

3 µW

volume

10 — 100 µm

Interfaces // Passive substrate// Processing technique (microstructure/ volume)

Outline

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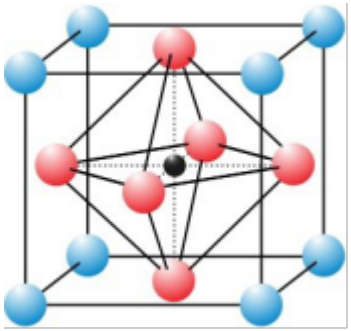
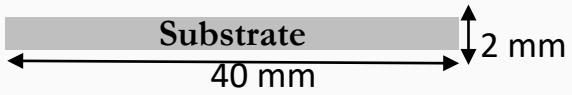
4. Conclusion



Screen-printed SS/Au/PZT/Au multilayer

1. **Pre-cut SS substrate (t=250µm)**



2. **Au Bottom electrode printing**

Drying at 120°C

Au: Paste (Au + glass)

3. **PZT layer printing**

Drying at 120°C

PZT = PZ26 (hard) Ferroperm + 3%wtLBCu(*)

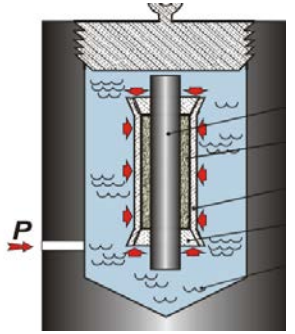
4. **Au Top electrode printing**

Drying at 120°C

(*)$Li_2CO_3Bi_2O_3CuO$

5. **Isostatic pressure**

40 MPa, 65 °C, 5 min



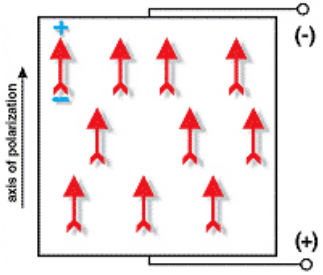
6. **Co-sintering Au/PZT/Au**

2h at 900 °C, 40°C/min

7. **Poling**

At 280°C <T_{curie}

50kV/cm, 5min



8. **Characterizations**

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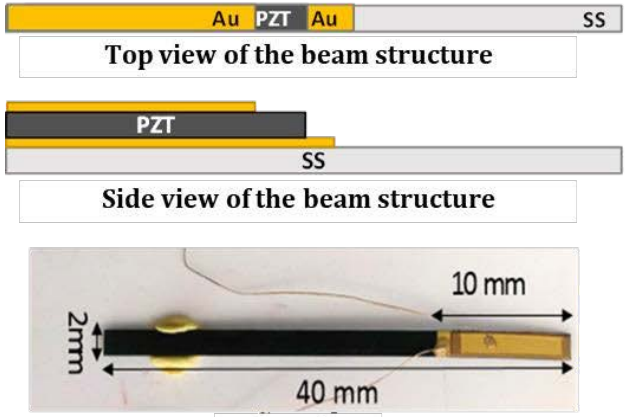
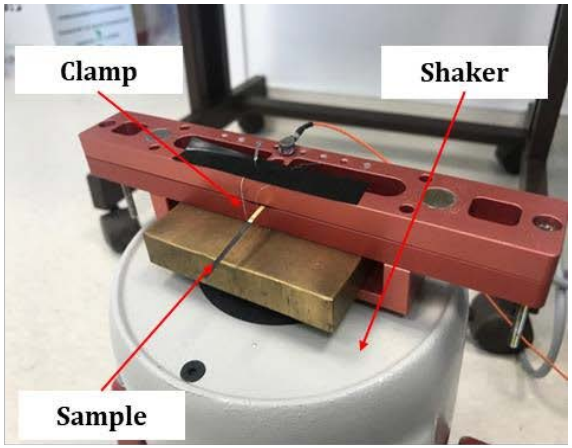
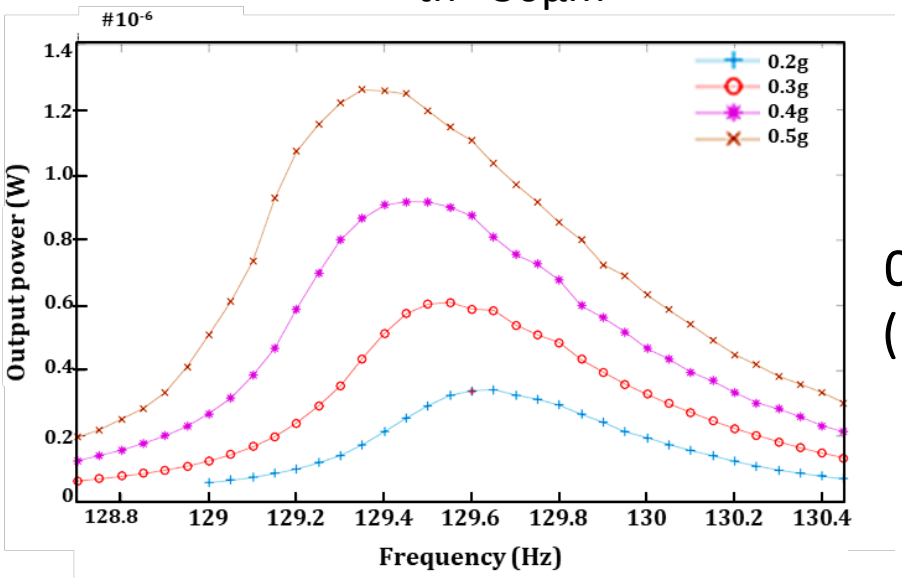
Screen-printed SS/Au/PZT/Au multilayer

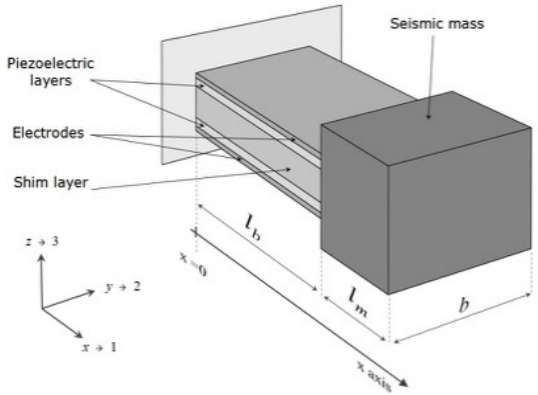


th≈ 50µm



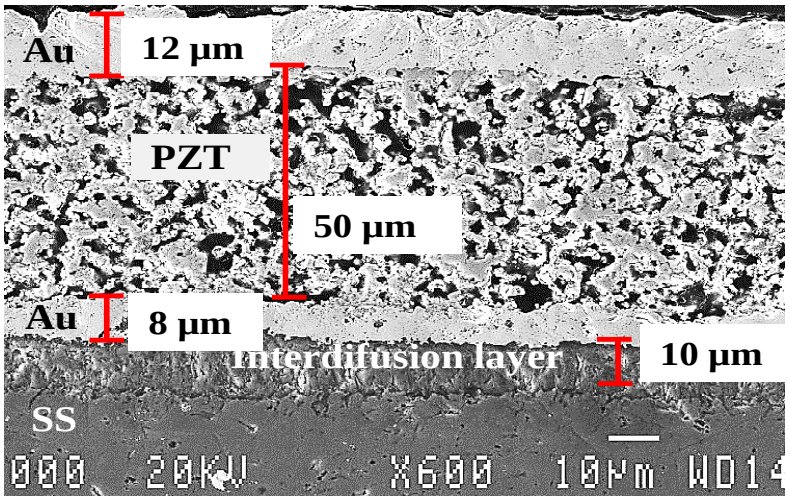


Max:
P = 1.3µW,
0.5g, f=129.2Hz
(Load = 2.7MΩ)



Mesures C2N University of Paris-Saclay (Conf. JNRSE 2019 Blois)

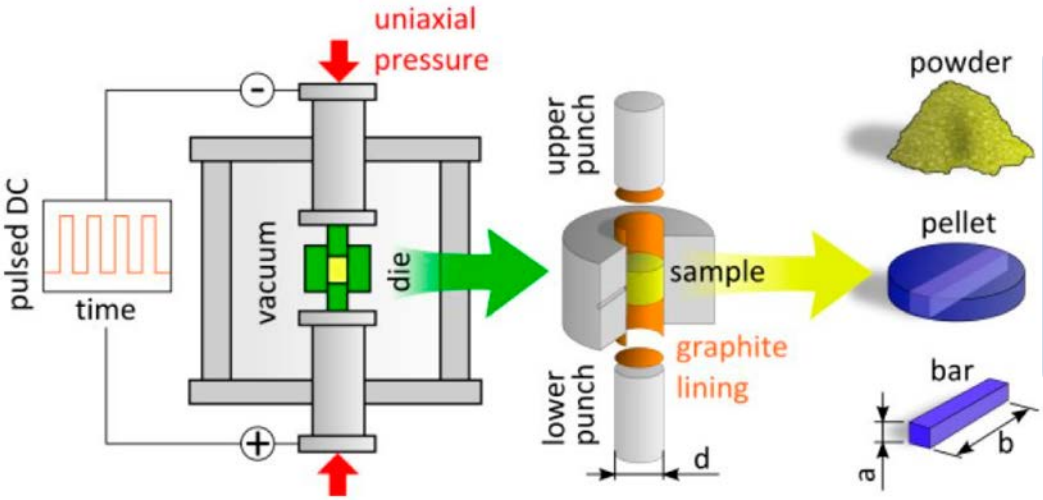
Screen-printed SS/Au/PZT/Au multilayer



- ✓ **Porosity 20% (> ceramics)**
- ✓ **Interdiffusion layer between SS substrate and bottom Au electrode**
- ✓ **Bending** (≠ CTE: SS301→18, Au →14, PZT →8 ppm/K)
- ✓ **Properties** : d_{31}~ – 40pC/N, (< ceramics)

→ SPS (Spark Plasma Sintering) approach on printed layers

(densification through combination of pressure + electrical current)

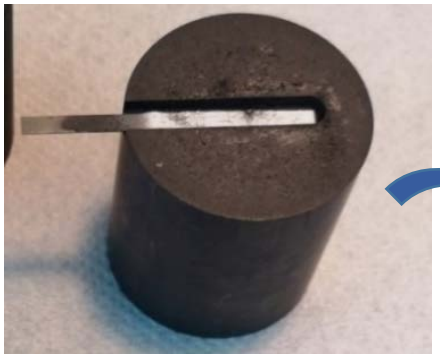


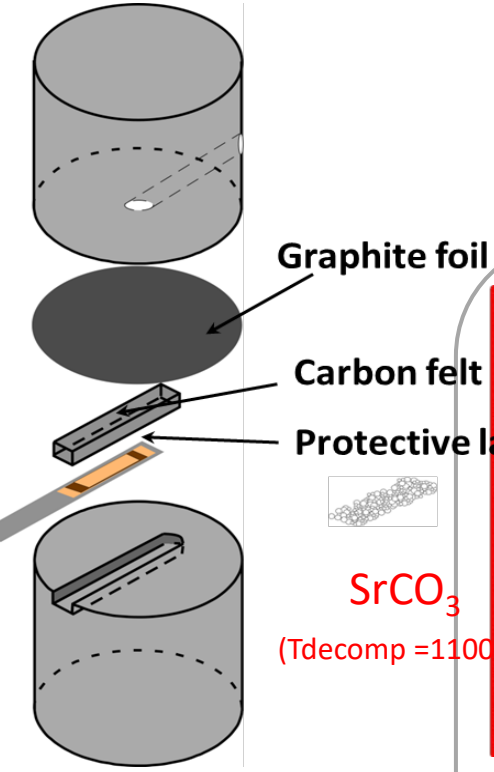
Advantages

- high densification rates
- one step for densification
- ↓ sintering temperature and duration (few minutes)⇒ ↓ energetic cost
- no sintering aid

SPS: transfer towards screen-printed PZT MEMS

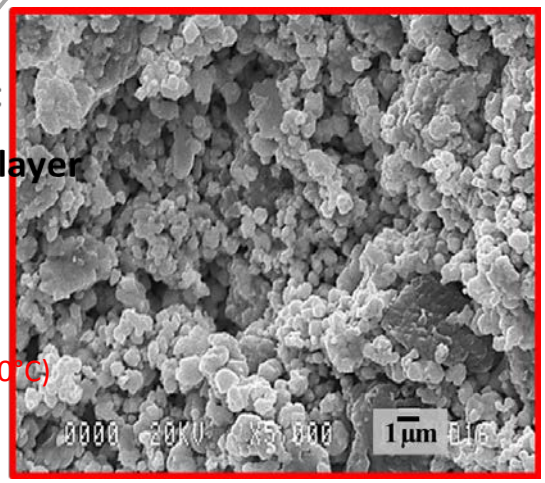
SPS MOULD ADAPTATION + USE OF PROTECTIVE LAYER





$SrCO_3$

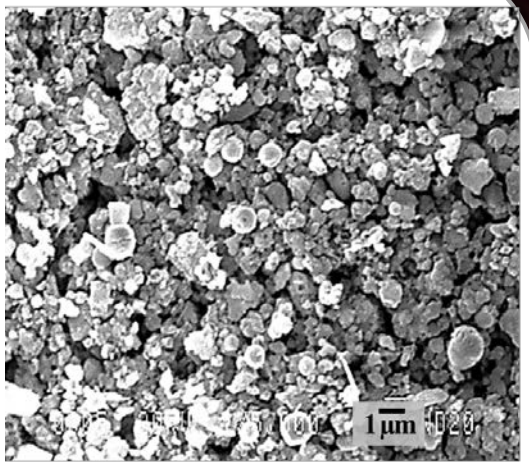
(Tdecomp =1100°C)



SPS

PZT (850°C, 5min)

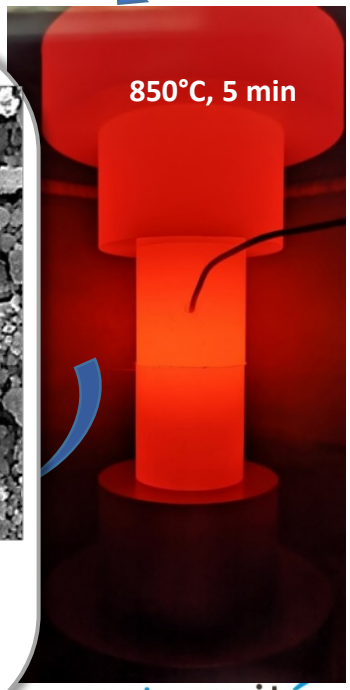
No sintering aid/no annealing



Conventional sintering

(900°C, 2h, 40MPa)

Sintering aid



Thèse Isabel Rua-Taborda, 2019

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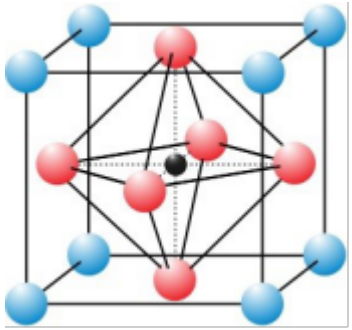

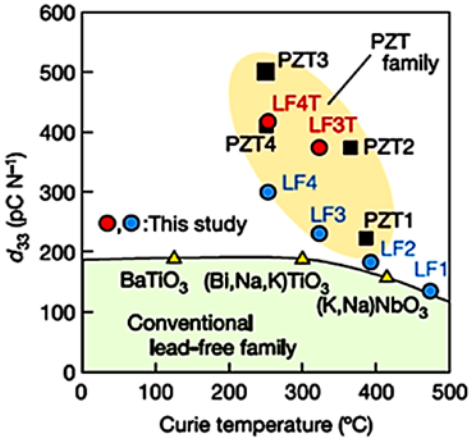

SAITO et al, Nature, 2004, Vol 432, p.84.

KNN piezo ceramic by SPS: state of the art

Reference	Sintering method	Sintering conditions	Grains size	Density	Post Annealing
1, 2014, Bah	SPS	920°C, 50 MPa 5', 100°C/min, Argon 950°C, 50 MPa 5', 100°C/min, Argon	2µm	96% 97%	900°C,5h under air
2, 2004, Birol	CS	1114°C, 2h 5°C/min Oxygen atmosphere	N/A	95,30%	N/A
3, 2006, Zuo	CS	1100°C, 4h, 300°C/h	N/A	98,00%	N/A
4, 2004, Wang	SPS	1100°C, 60 MPa, 3', 150°C/min vaccum	2-6µm	98%	950°C,5h
5, 2021, Gomes	SPS	1000°C, 50 MPa, 20', 100°C/min	3µm	96%	900°C,5h under air

remove residual graphite /oxygen vacancies

Conventional Sintering CS **Tsint. > 1100°C**

Spark Plasma Sintering SPS **Tsint. : 920 -1100°C** **+ post annealing 900°C**

1. Bah, M., Ceramics International (2014). doi:10.1016/j.ceramint.2013.12.097
2. Birol, H., Journal of the European Ceramic Society (2006). doi:10.1016/j.jeurceramsoc.2004.11.022
3. Zuo, R., J American Ceramic Society (2006). doi:10.1111/j.1551-2916.2006.00991.x
4. Wang, R Materials Research Bulletin (2004). doi:10.1016/j.materresbull.2004.05.007
5. Gomes, M. M., Ceramics International (2021). doi:10.1016/j.ceramint.2020.11.192

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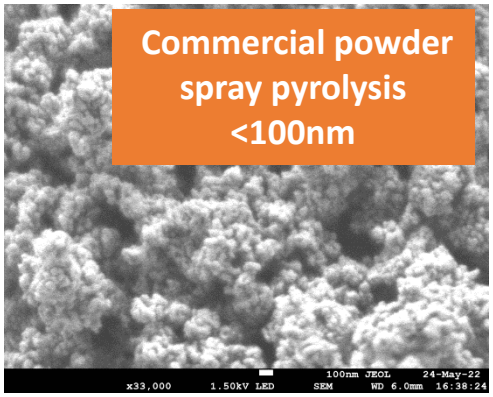
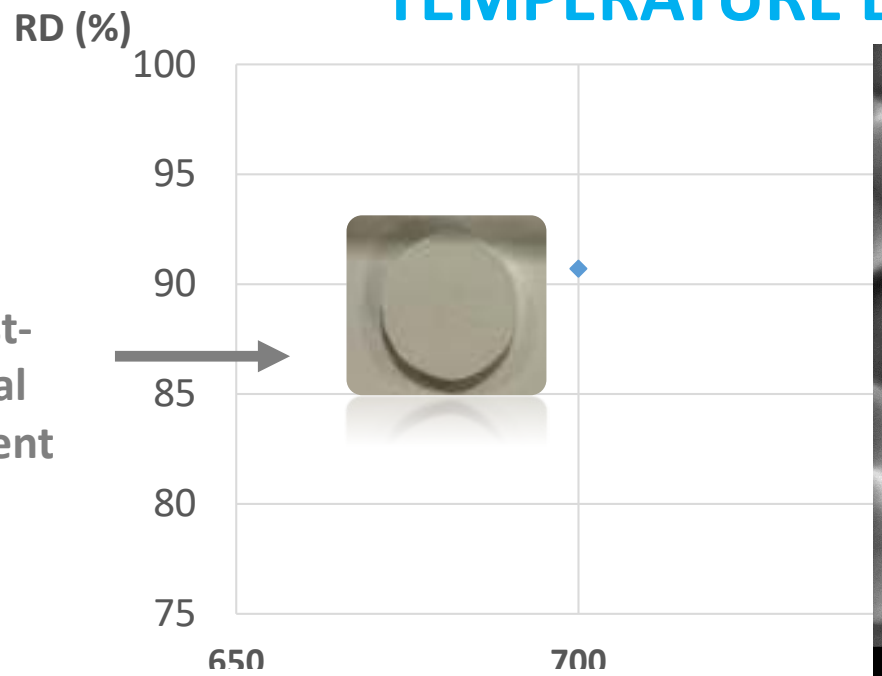
From KNN nanopowders to piezo ceramic by SPS

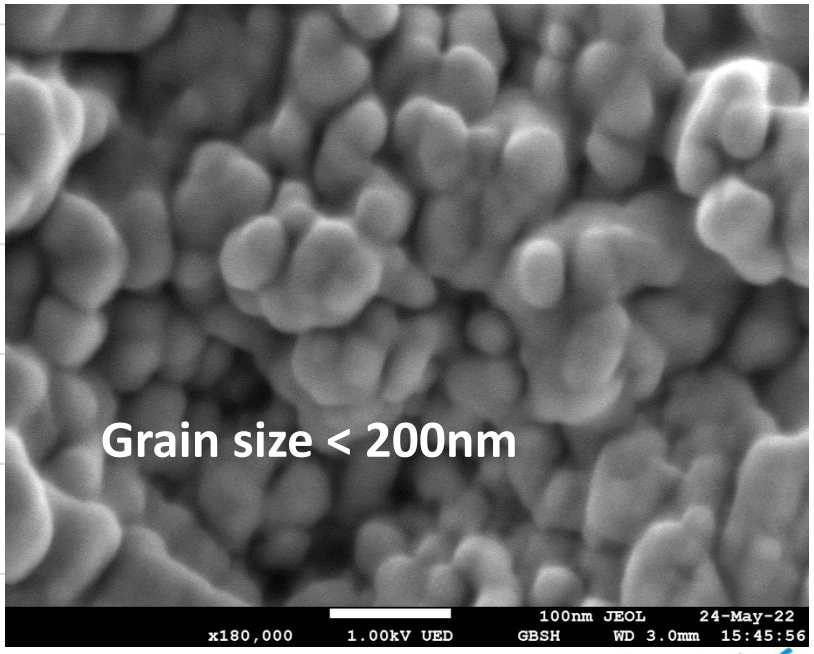


40MPa, 100°C/min

TEMPERATURE EFFECT (5min)



No post-thermal treatment



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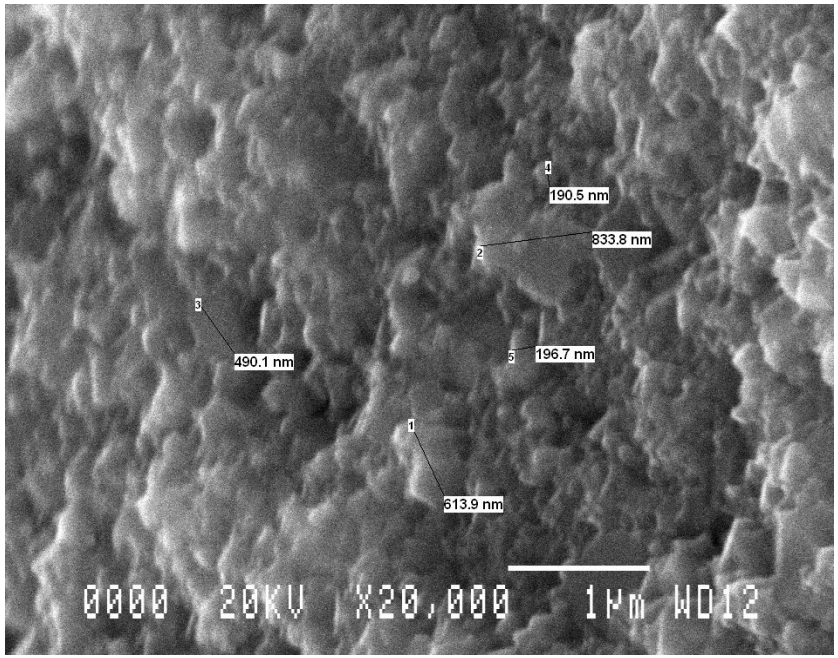
From KNN nanopowders to piezo ceramic by SPS

STRATEGIES TO AVOID ANNEALING WHILE INCREASING Tsint

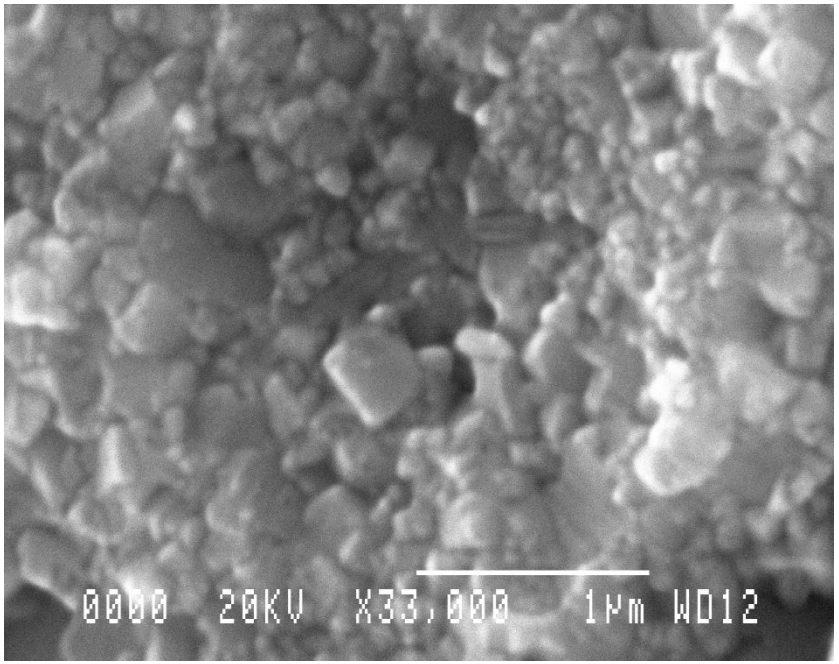
Protective layer $SrCO_3$



750°C 40MPa 5' 100°C/min – 94%

$SrCO_3$/KNN/$SrCO_3$

Thermal ramps



750°C 40MPa 5' 200°C/min - 97%

(200-500nm)

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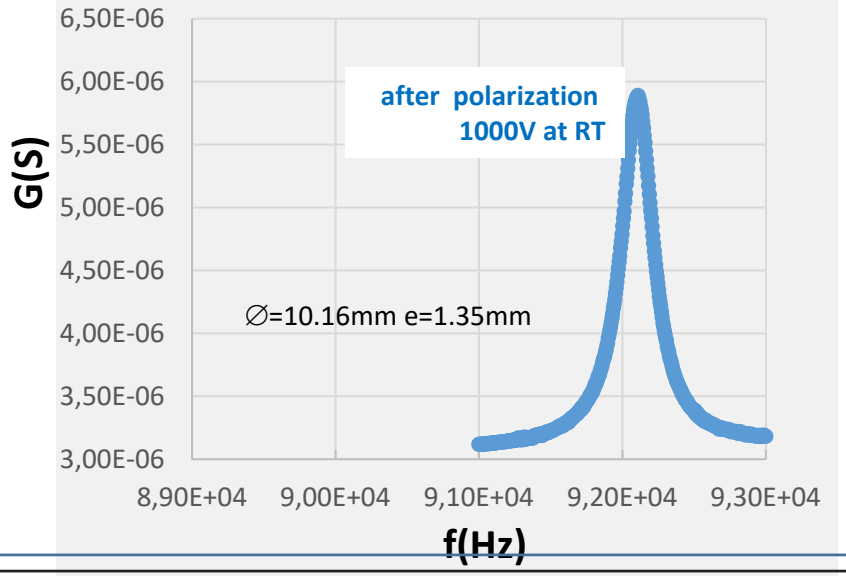
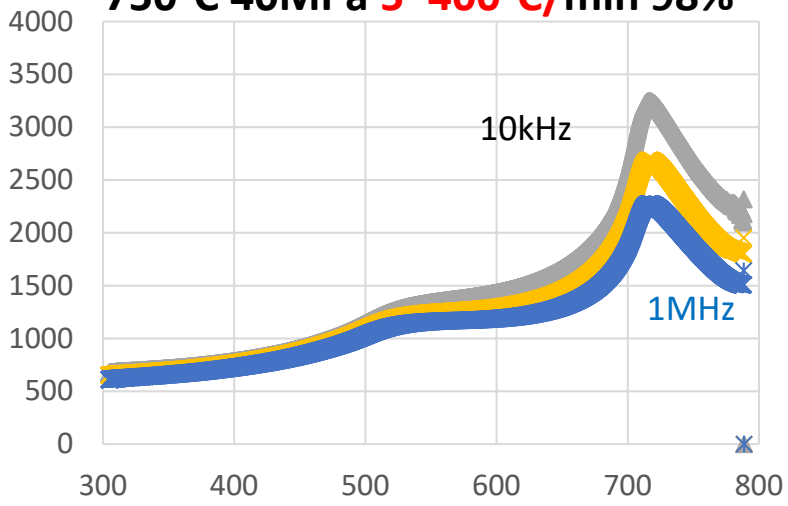
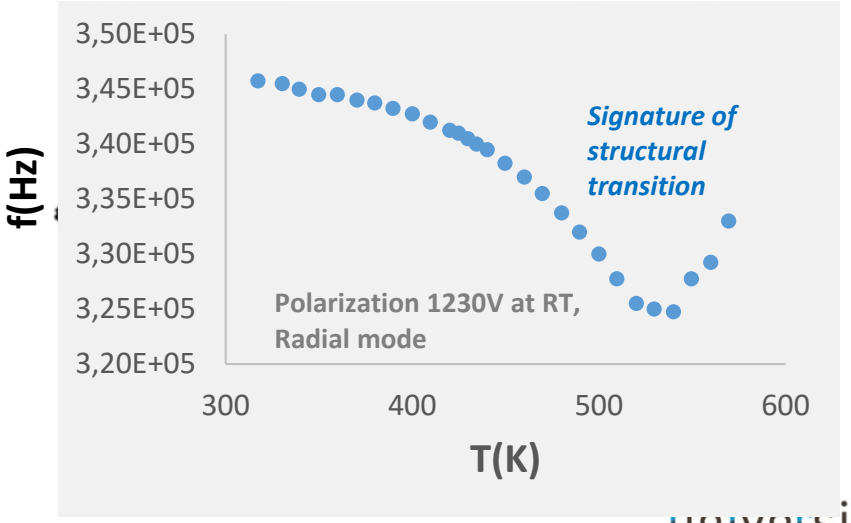
From KNN nanopowders to piezo ceramic by SPS

700°C 40MPa 15'100°C/min 90%



750°C 40MPa 5' 400°C/min 98%





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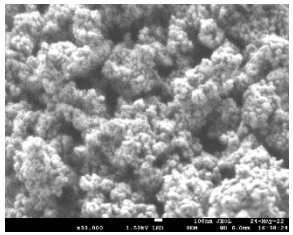
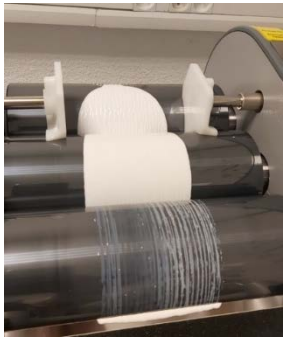
From KNN nanopowders to thick film

Paste preparation



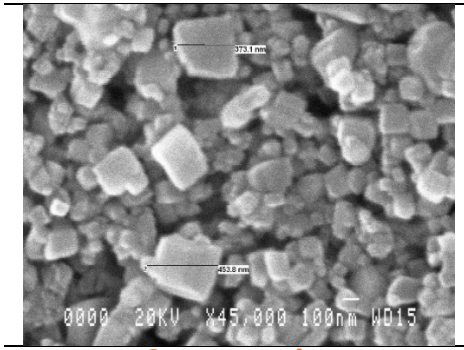
1. **Drying**
2. **Sonication**
3. **Mix with cellulosic binder (~50%wt)**
4. **Three roll miller**



Printed layers

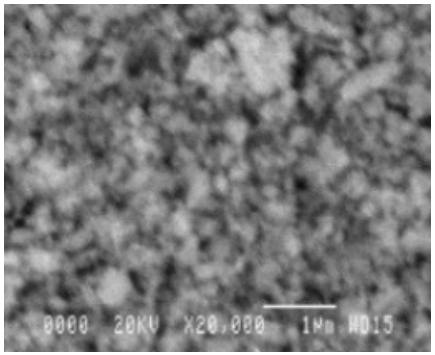
Printed layer on stainless steel substrate

Microstructure (2h, 900°C)



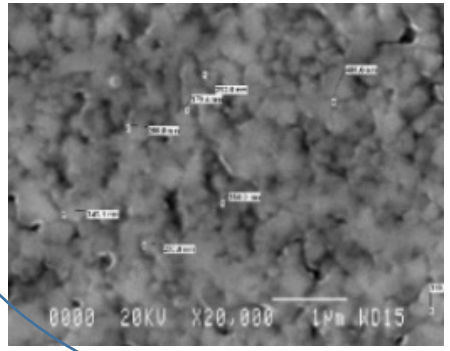
Top view

Cross section



200 <Grains size<500nm

Cross-section (pressed)



Pressure step mandatory

Isostatic, 40MPa, 65°C

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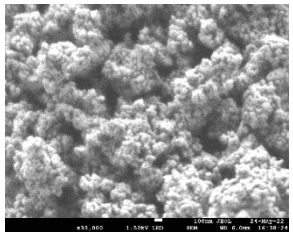
From KNN nanopowders to thick film

Paste preparation



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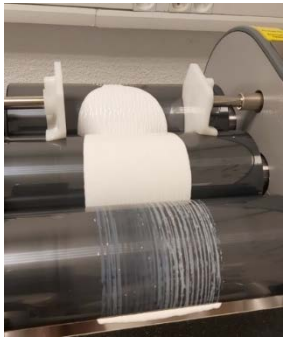
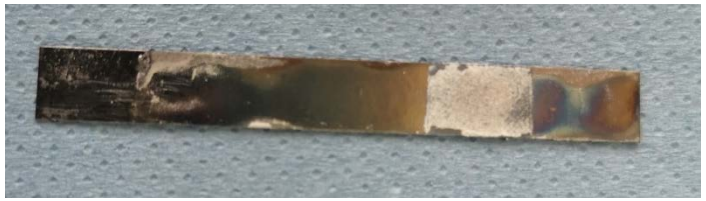
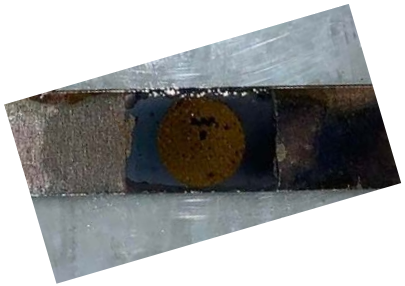


Printed layers and SPS





After $SrCO_3$ phosphoric acid attack

700°C – 10 min – $SrCO_3$ Au/KNN/Au/Inox

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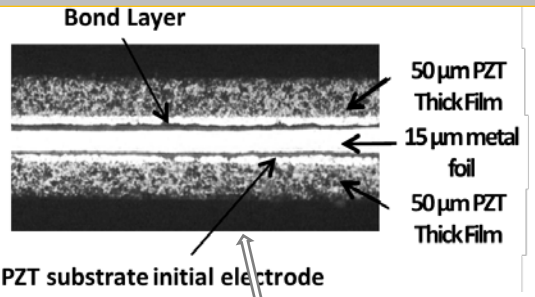
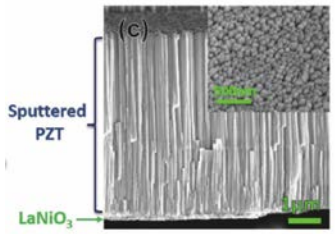
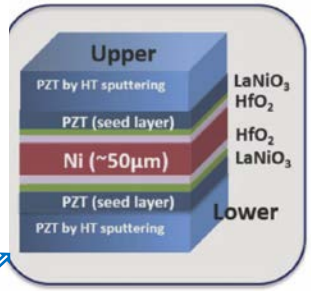
Conclusion/Perspectives

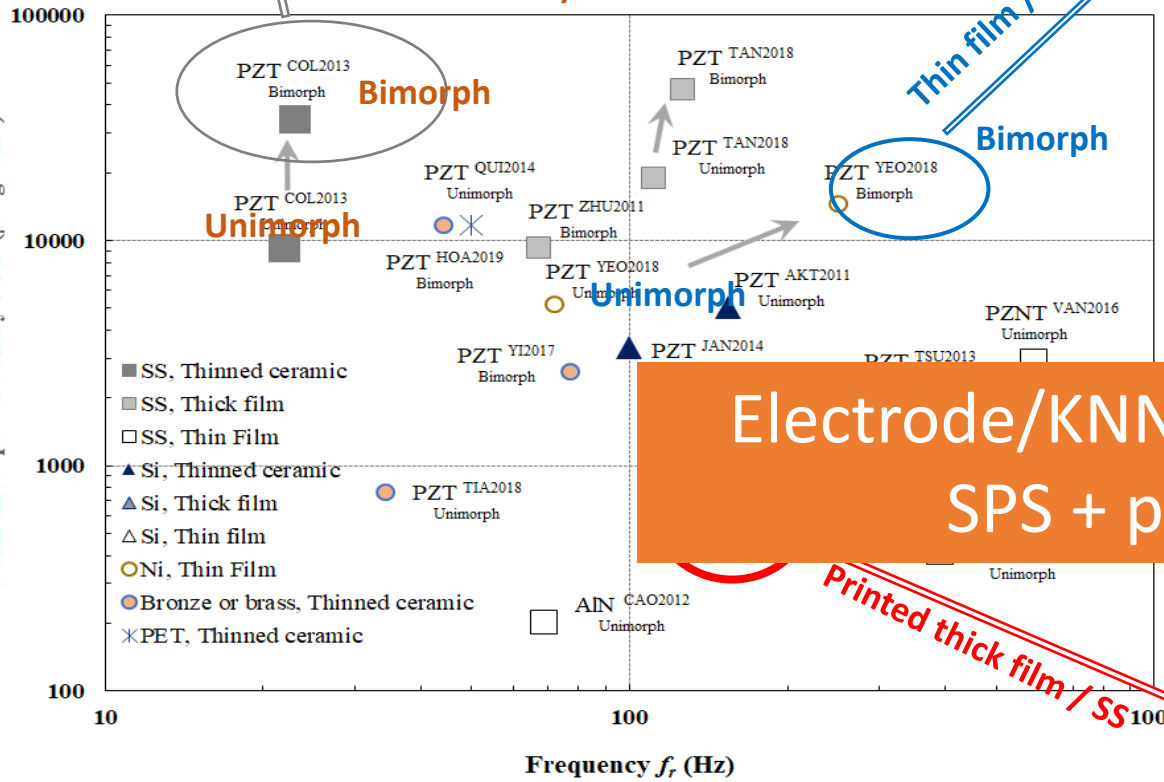


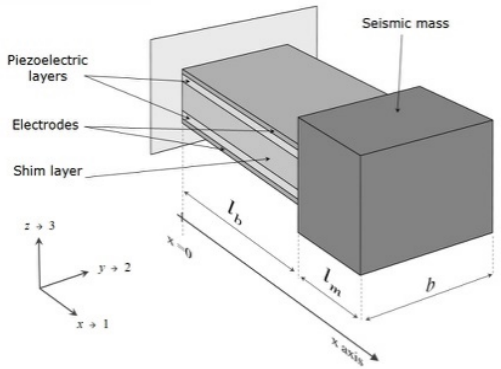
Thinned ceramic /SS





Thin film / Ni





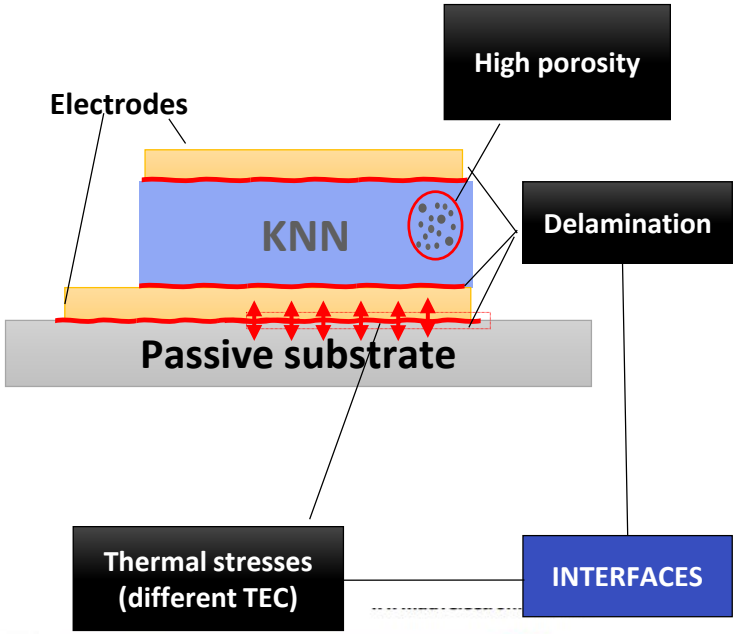
Printed thick film / SS

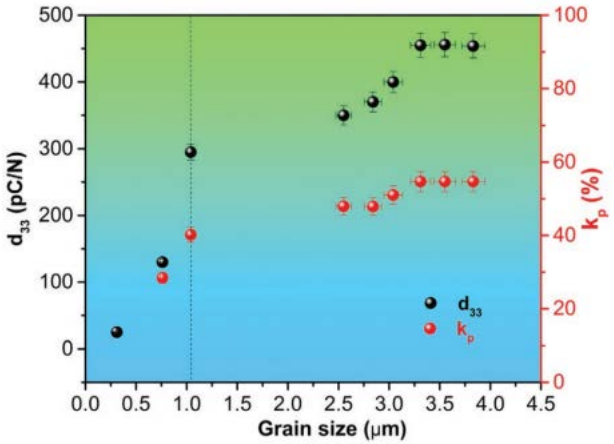
Electrode/KNN/electrode/SS: SPS + printing?

(livre blanc GDR Name)

P = 1.3µW, 0.5g, f=130Hz

Conclusion /Perspectives





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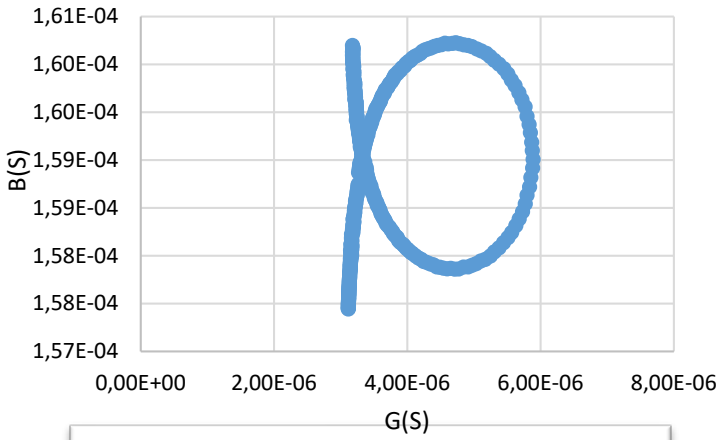
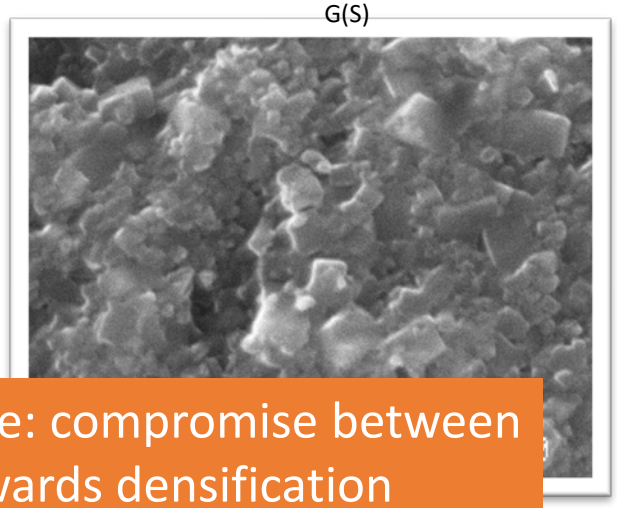
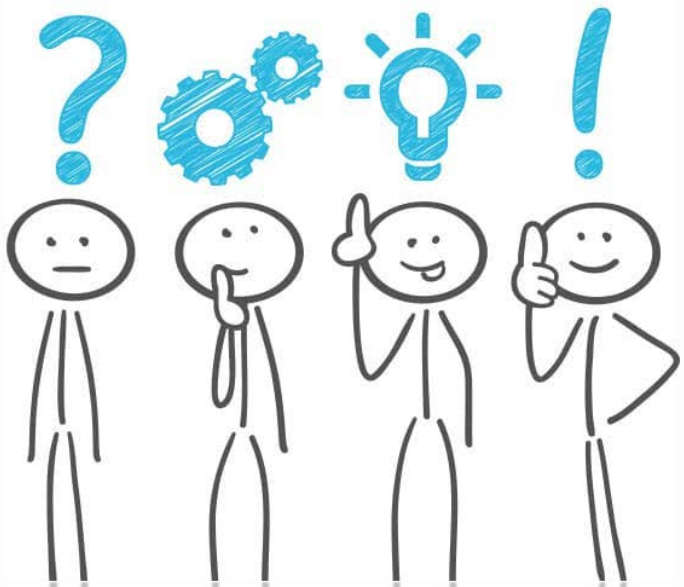
SPS: 700°C 40MPa 15'100°C/min 90.2%





KNN grain size: compromise between reactivity towards densification versus impact on properties

Towa ping and sir vskite powd thick



[1]Université de Bordeaux, Laboratoire IMS, Talence, France

[2]Laboratoire ICMCB, CNRS, Pessac, France

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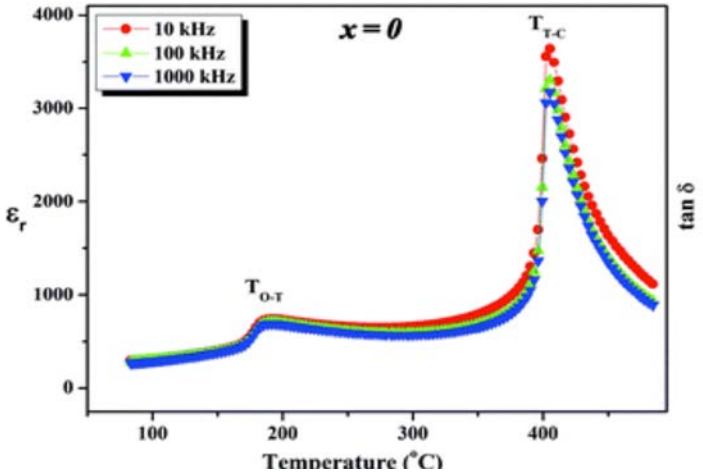

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orthorhombic to tetragonal and tetragonal to cubic phase transitions