10-3-2017

ENVIRONMENTALLY FRIENDLY PROCESSING OF LEAD FREE SODIUM POTASSIUM NIOBATE THICK FILMS BY ELECTROPHORETIC DEPOSITION

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Environmentally friendly processing of lead free KNN thick films by EPD

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This is a team work

TEAM WORK

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Morgane Dolhen

Rui Pinho

M. Elizabete Costa

- There is a need …
- Our approach
- Our results
- What I´ve just said ···

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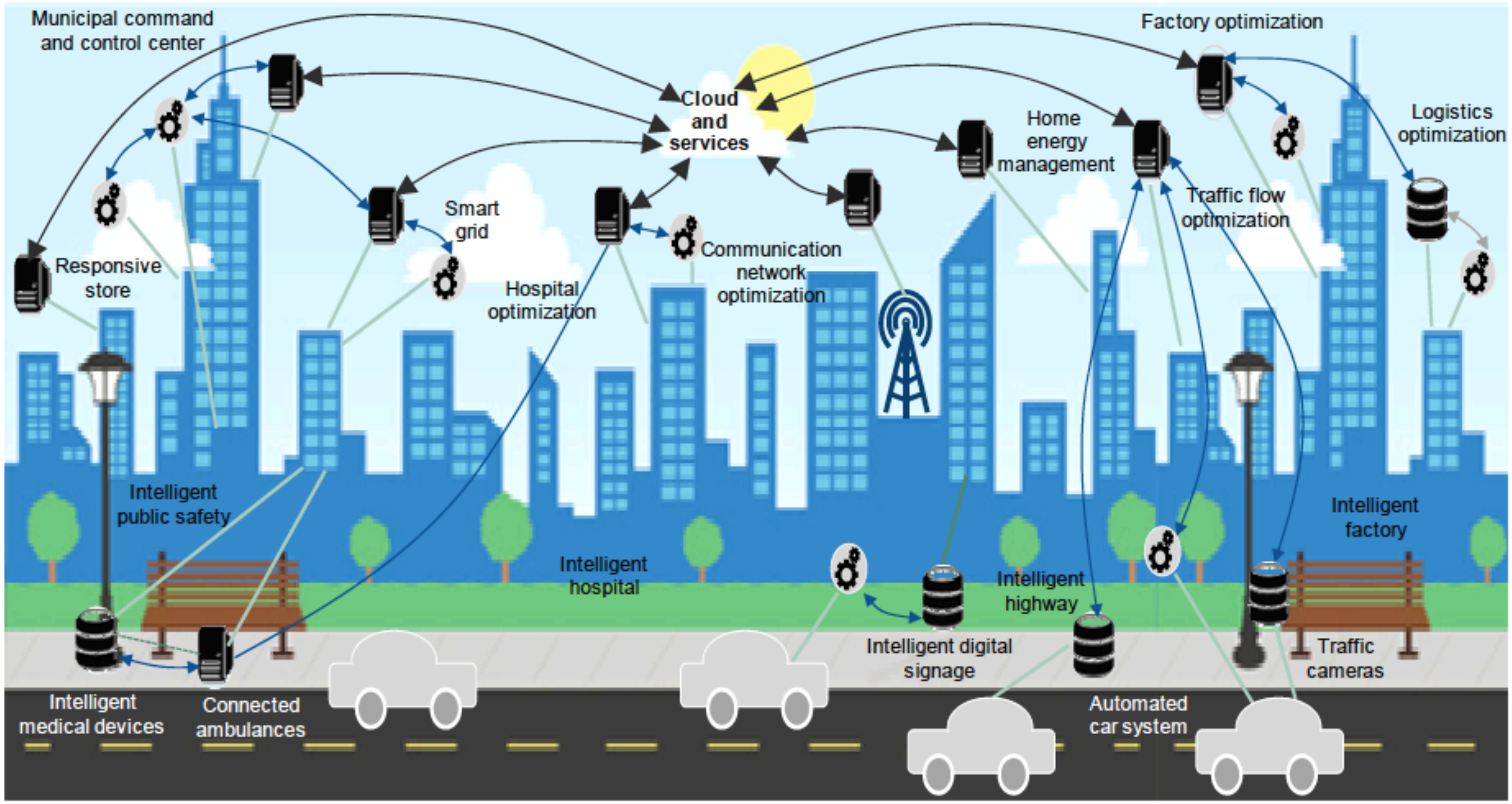
Sustainable World

Smart World

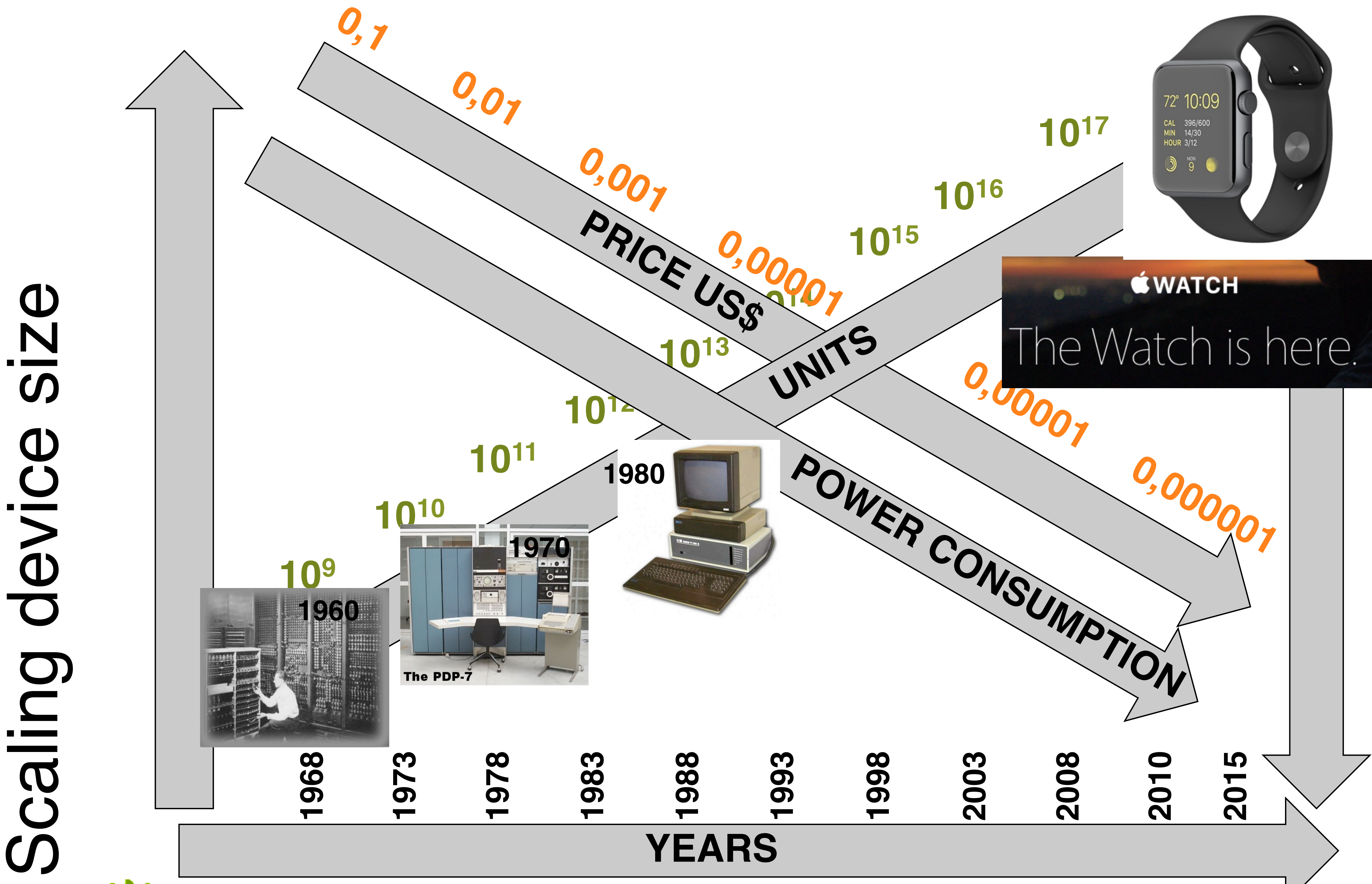
THE WORLD IN 2025
10 PREDICTIONS OF INNOVATION, by Thomson Reuters

A City with a Digital Overlay

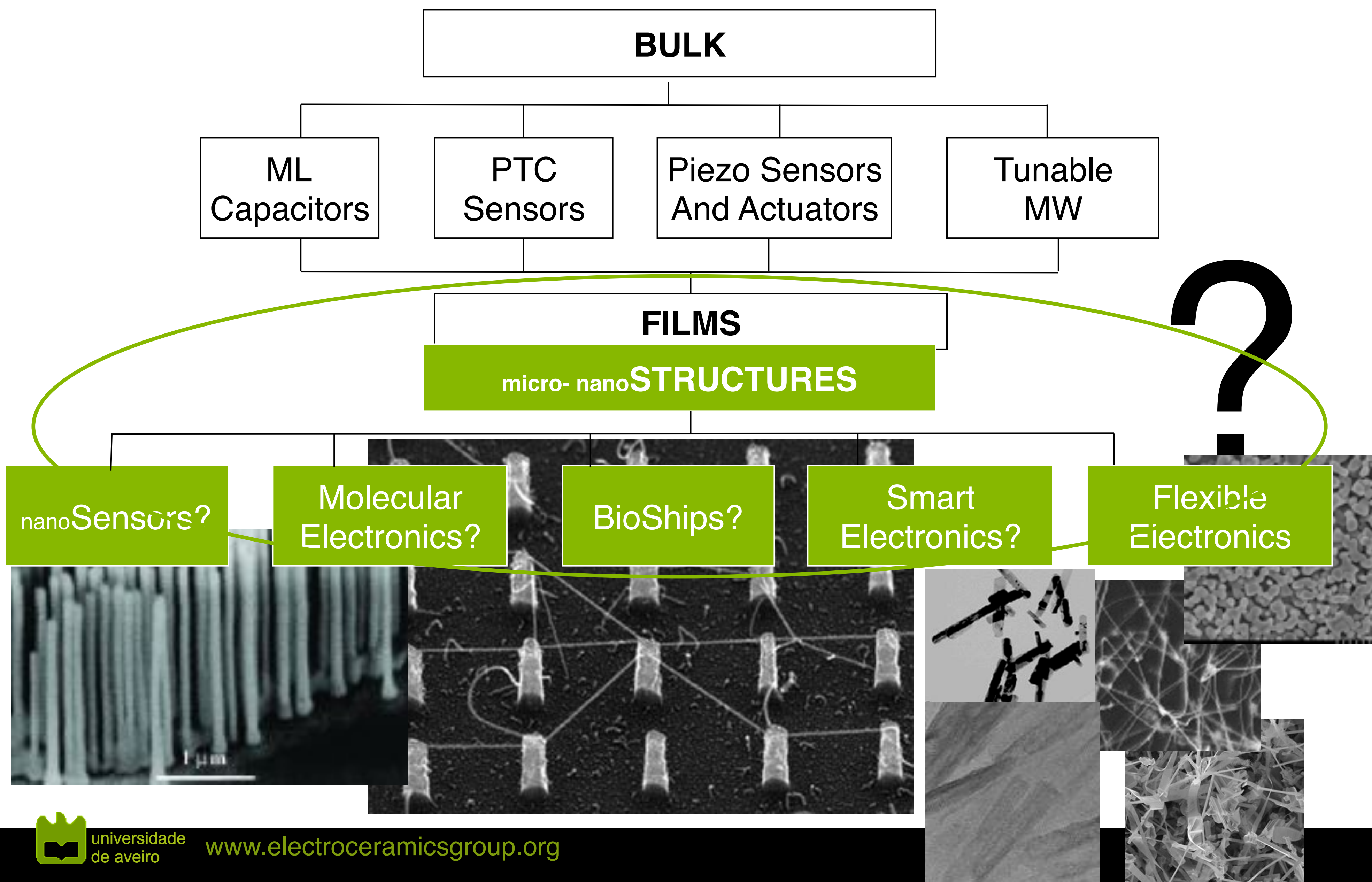


Source: IDC Government Insights, 2013

In 2020, 212 billion things will be talking to each other …


Scaling device size
0,1
0,01
0,001
0,00001
0,000001
0,0000001
PRICE US$
10^9
10^{10}
10^{11}
10^{13}
10^{15}
10^{16}
10^{17}
UNITS
POWER CONSUMPTION
1960
1970
The PDP-7
1980
72° 10:09
CAL 396/600
MIN 14/30
HOUR 3/12
WATCH
The Watch is here.
1968
1973
1978
1983
1988
1993
1998
2003
2008
2010
2015
YEARS

Electrofunctional nanoStructures

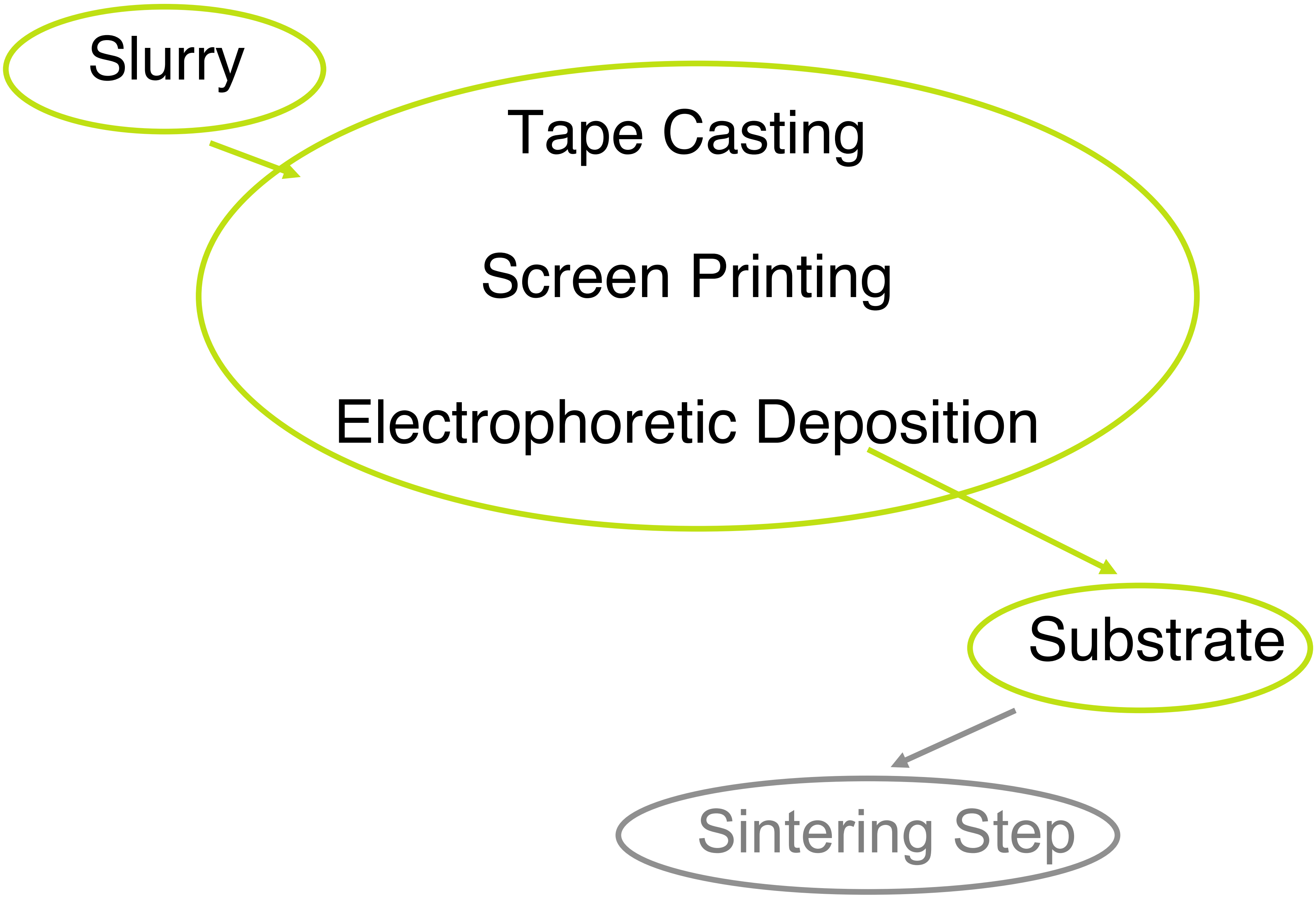


Films and Thick Films

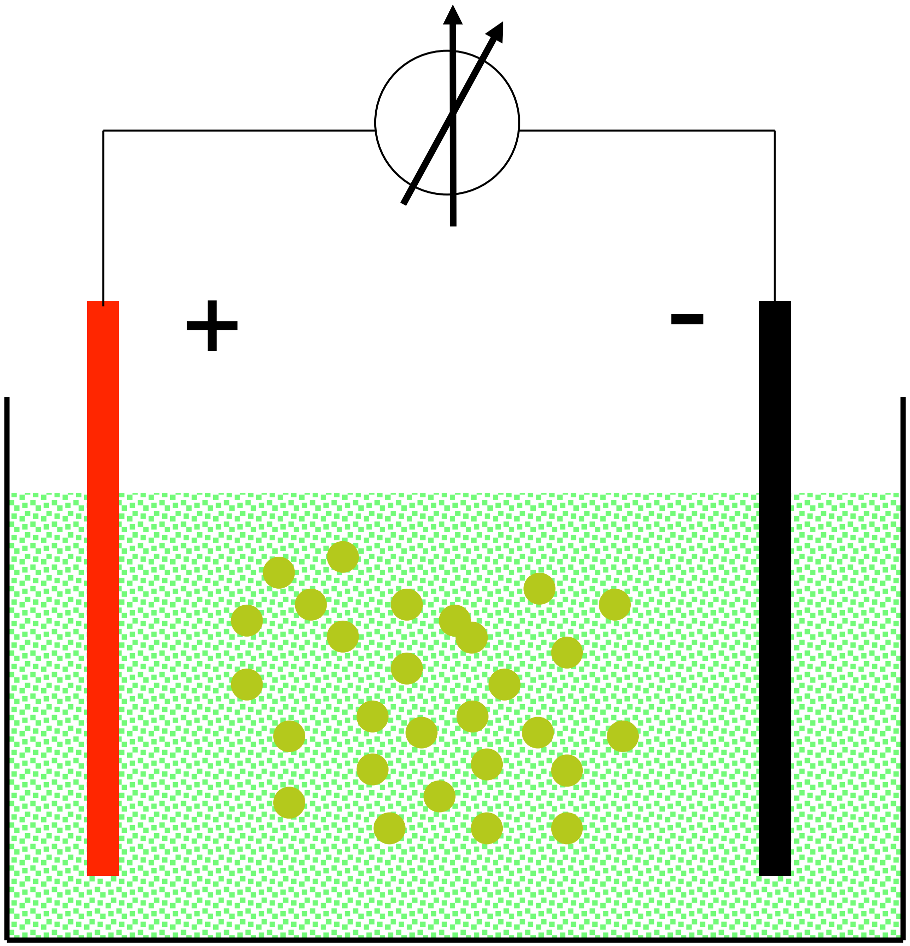
Thin Film Techniques	Thick Films Techniques
Physical Vapour Deposition	Tape casting
Sputtering (rf magnetron, dc, ion beam)	Screen printing
Evaporation (e-beam, resistance, molecular beam epitaxy)	Electrophoretic deposition
Laser Ablation	Hybrid sol-gel technique
Chemical Deposition	
Chemical Vapour Deposition	
MOCVD (Metal-organic CVD)	
PECVD (plasma-enhanced CVD)	
LPCVD (low pressure CVD)	
ALD (atomic layer deposition)	
Chemical Solution Deposition	
Sol-gel (solution gelation)	
MOD (metallorganic deposition)	
Langmuir–Blodgett	

Thin films $< 1\ \mu m$
Thick films $> 1\ \mu m$

Thick films preparation



Electrophoretic Deposition



EPD technique

Thick films preparation

Tape Casting	Free standing films	Until mm
Screen Printing	Flexible and rigid substrates	Until mm
EPD	Metal or metal covered substrates **Conformal shaping**	>1μm <50μm

P. M. Vilarinho et al, Recent Research Developments in Materials Science, 5, 1-24, Research Sign Post, 2004 (ISBN: 81 – 7736 – 203 – 8)

Thick films preparation

Tape Casting	Free standing films	Unti
Screen Printing	Flexible and substrates	Until mm
EPD	Metal al covered sub **C mal shaping**	>1μm <50μm

Absence of binders and ligants ...

P. M. Vilarinho et al earch Developments in Materials Science, 5, 1-24, Research Sign Post, 2004 (736 – 203 – 8)

EPD advantages :

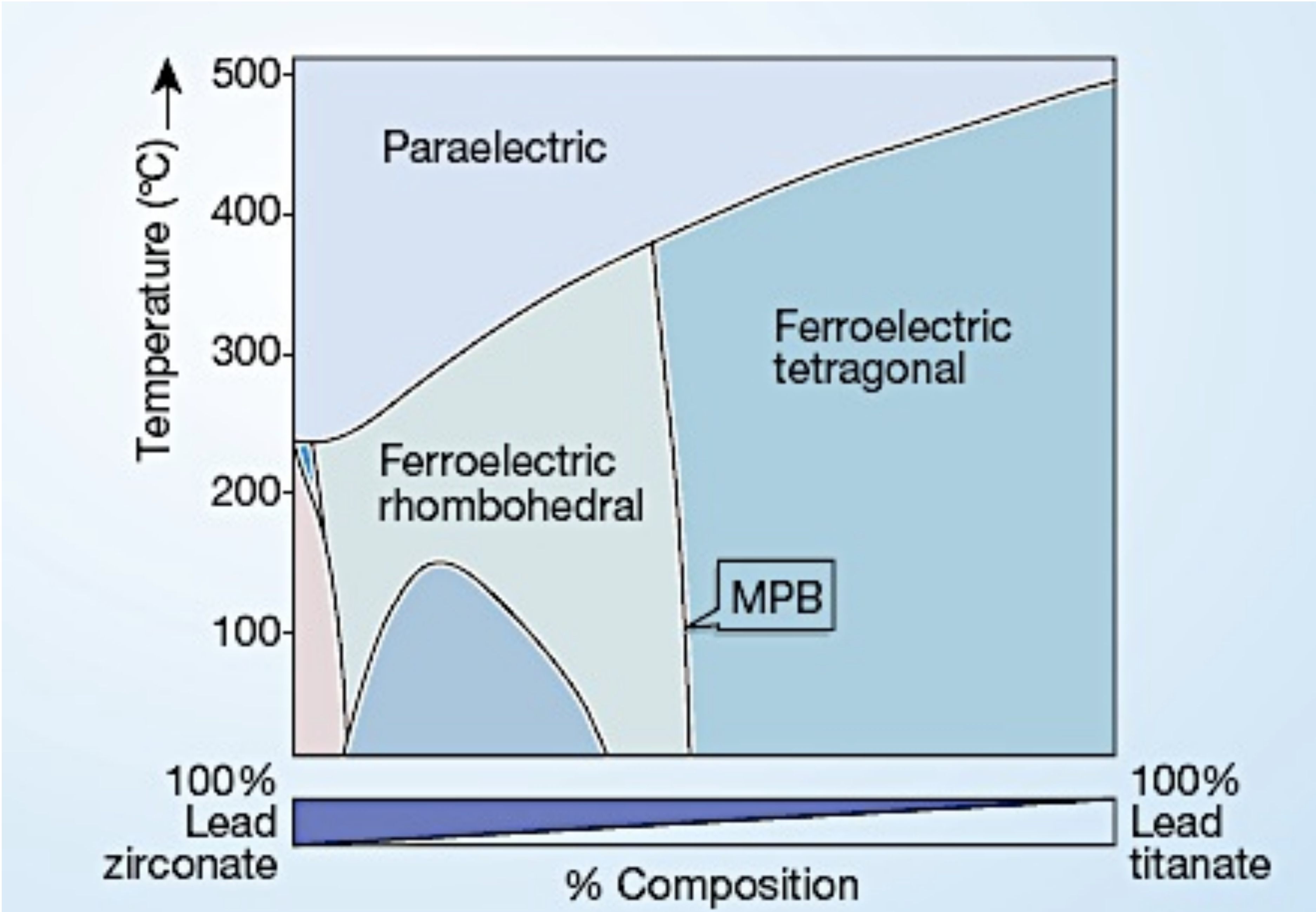
- High flexibility and simplicity
- Complex conformal patterns
- Cost effectiveness
- Embedding integration
- Ability to deposit large areas
- Ability to be scaled up
- Suitable for fabrication of thin films
- Applications in nanotechnology

I. Corni, M. P. Ryan, A. R. Boccaccini, Journal of the European Ceramic Society, 28, 1353, 2008

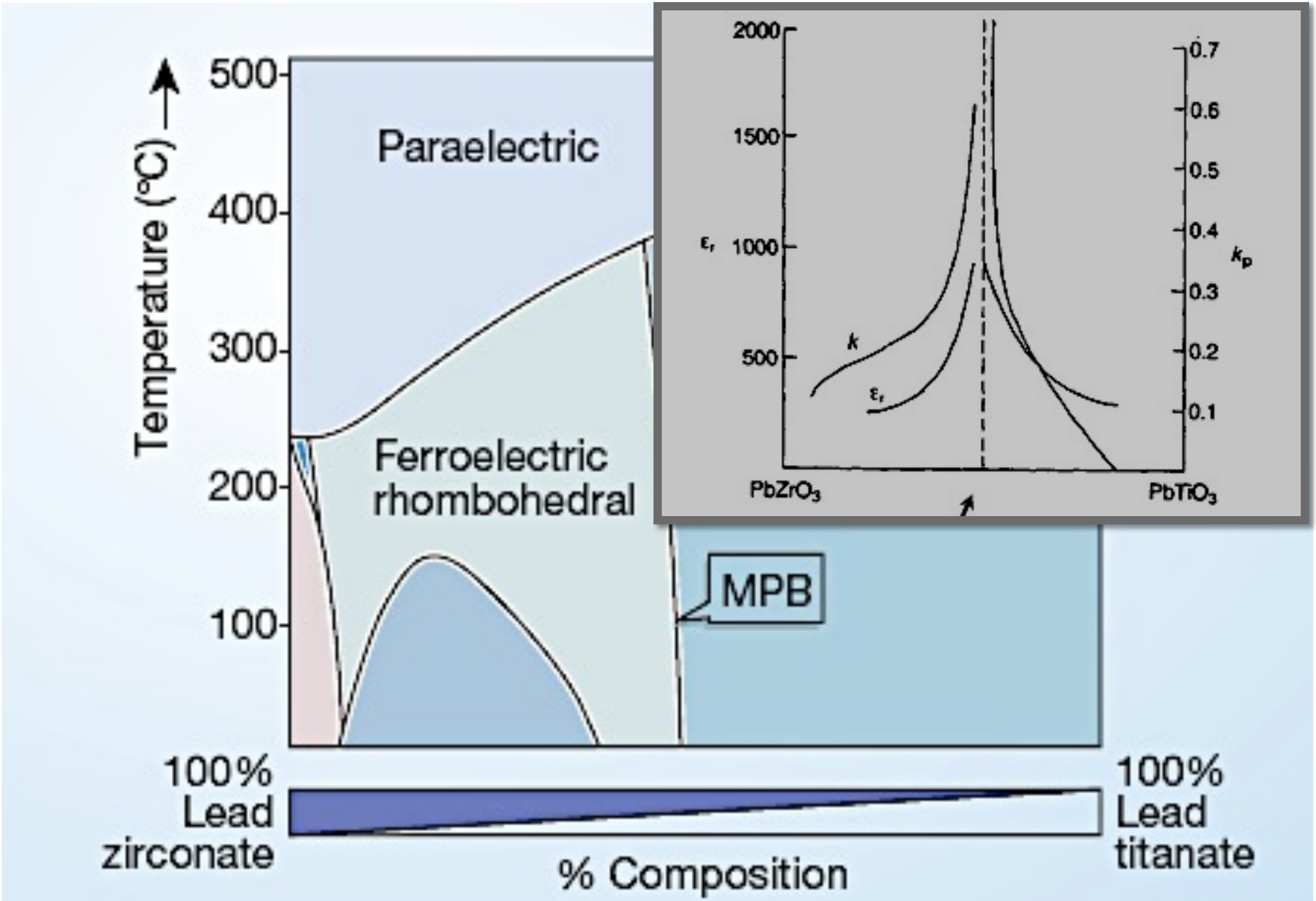
Piezoelectrics


D'OH!
RUN!
HERCULANEUM, MO
CONTAMINATED SINCE
1892
LEAD WASTE
DECONTAMINATION
DOE R
© MATSON
APOLOGIES TO MATT GROENING
ST. LOUIS POST-DISPATCH
caglecartoons.com

$PbZrO_3 - PbTiO_3$

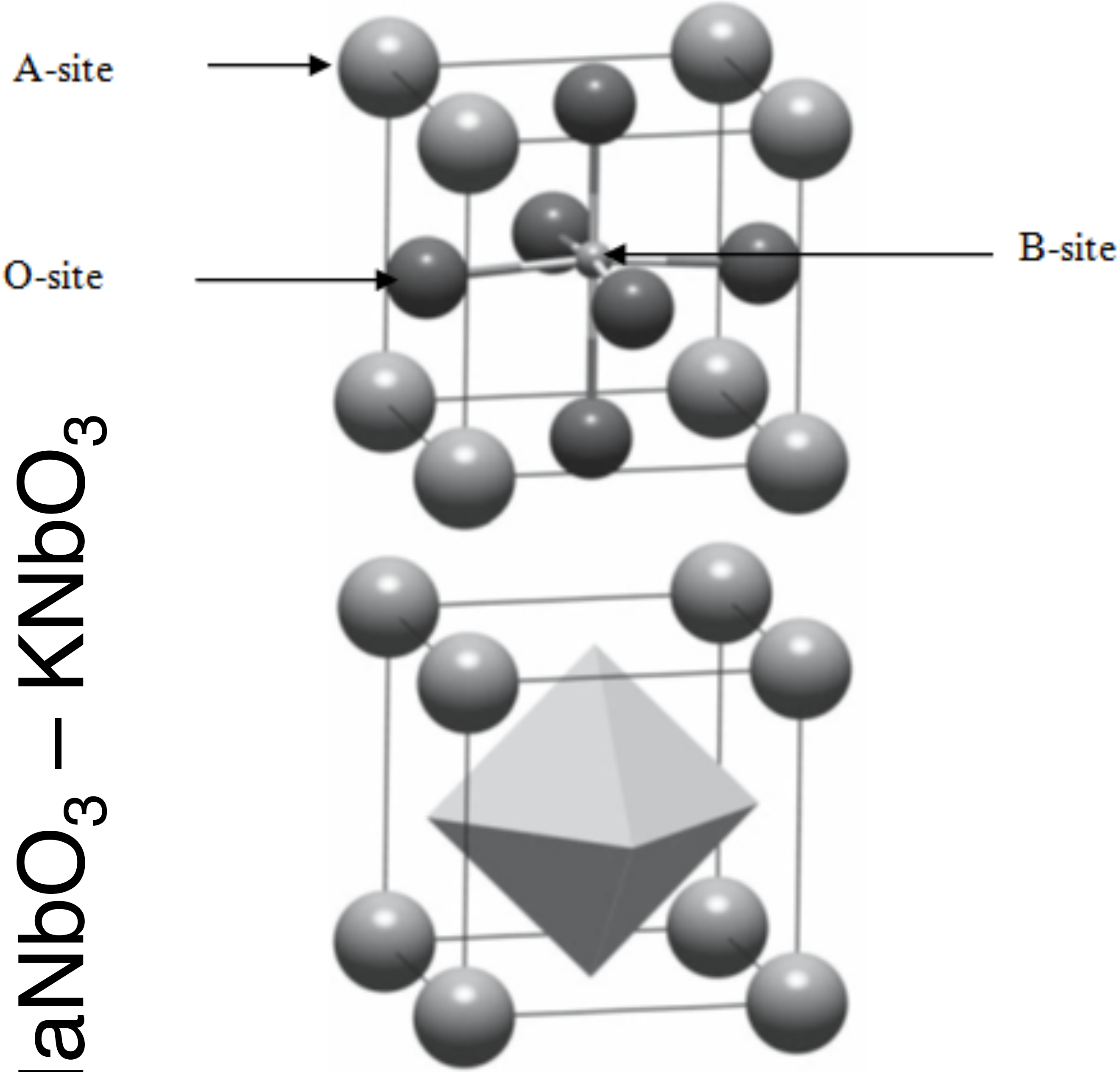


$PbZrO_3 - PbTiO_3$

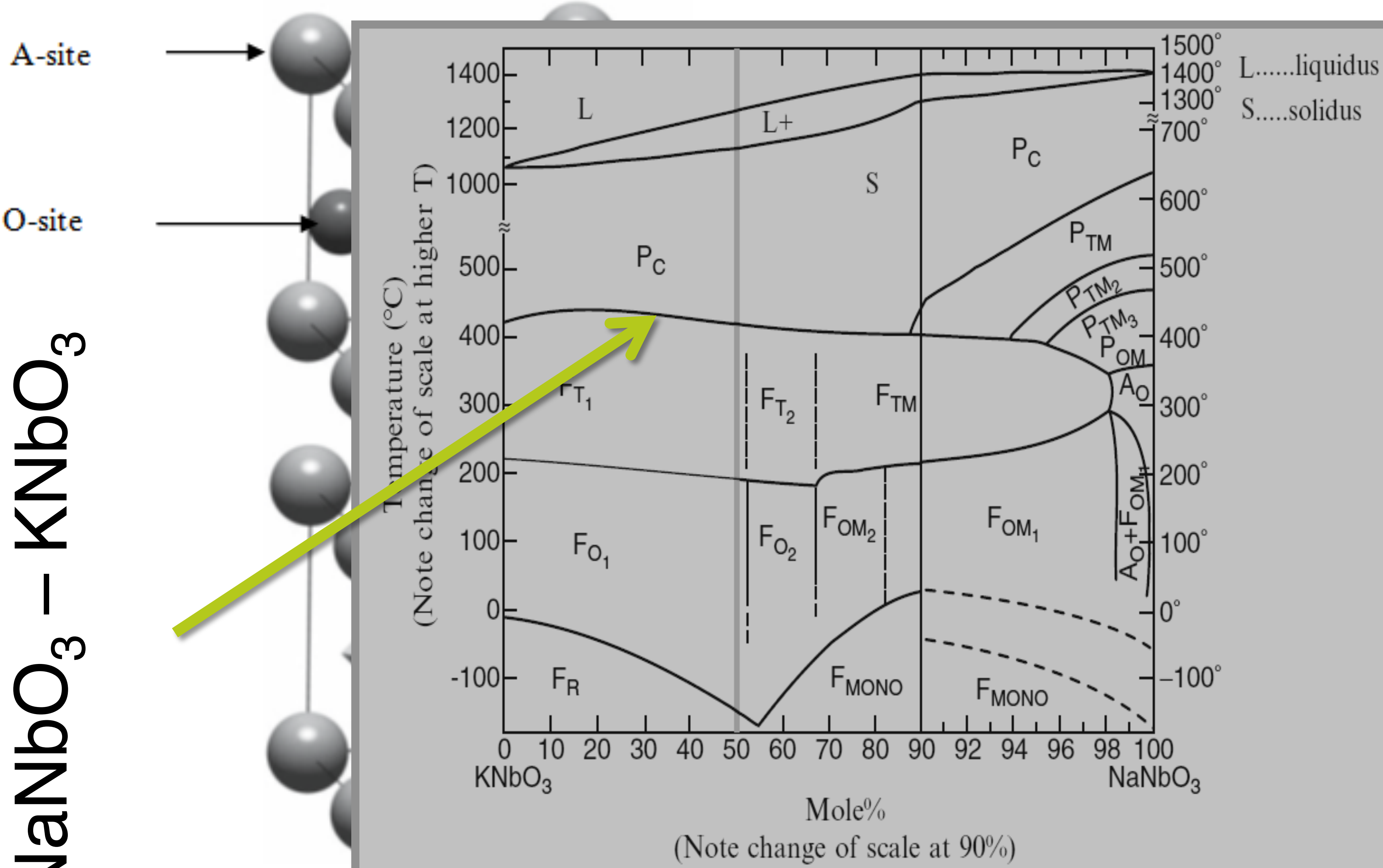


Lead free piezoelectrics $NaNbO_3$ – $KNbO_3$ (KNN)

$NaNbO_3 – KNbO_3$

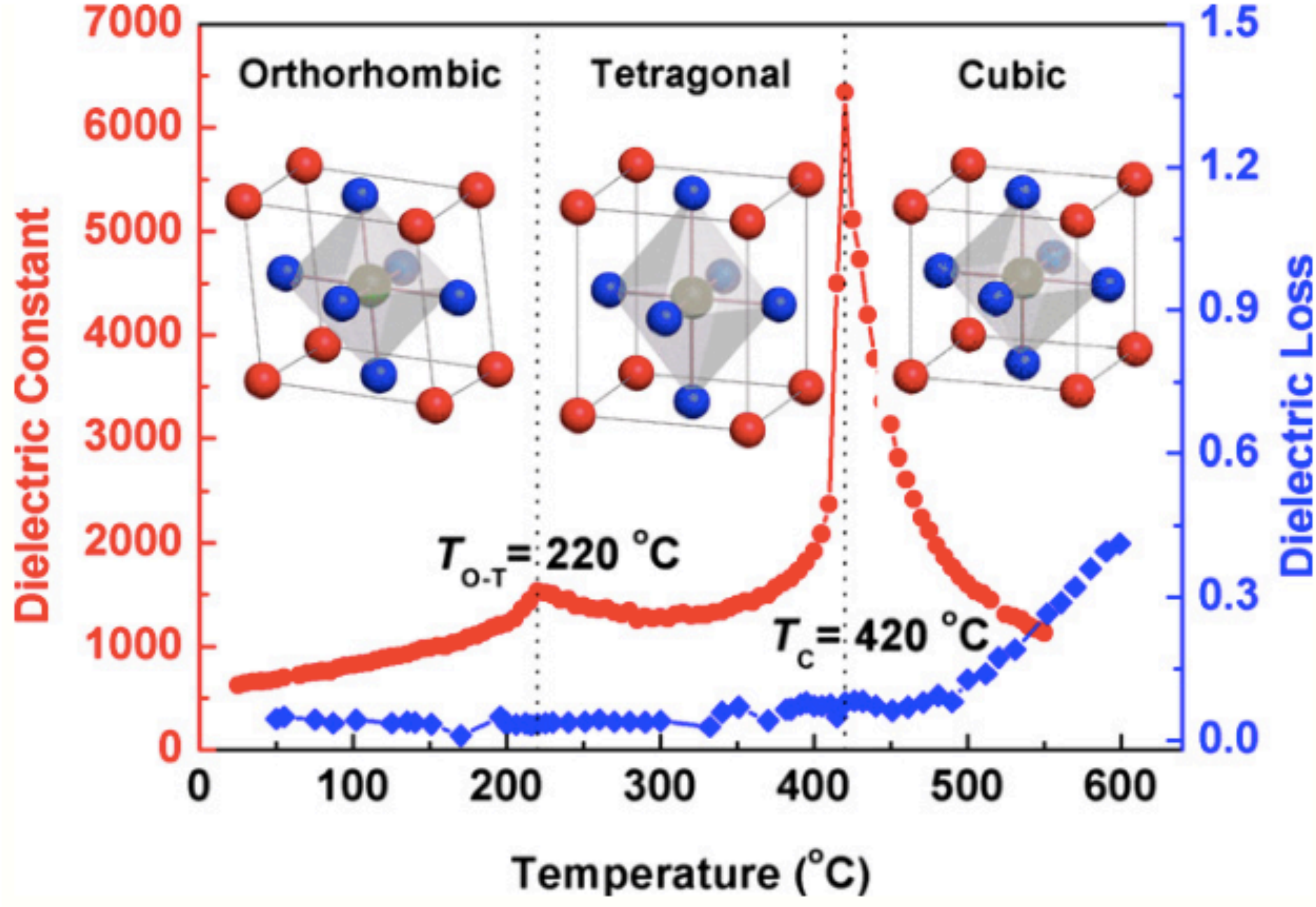


$NaNbO_3 – KNbO_3$



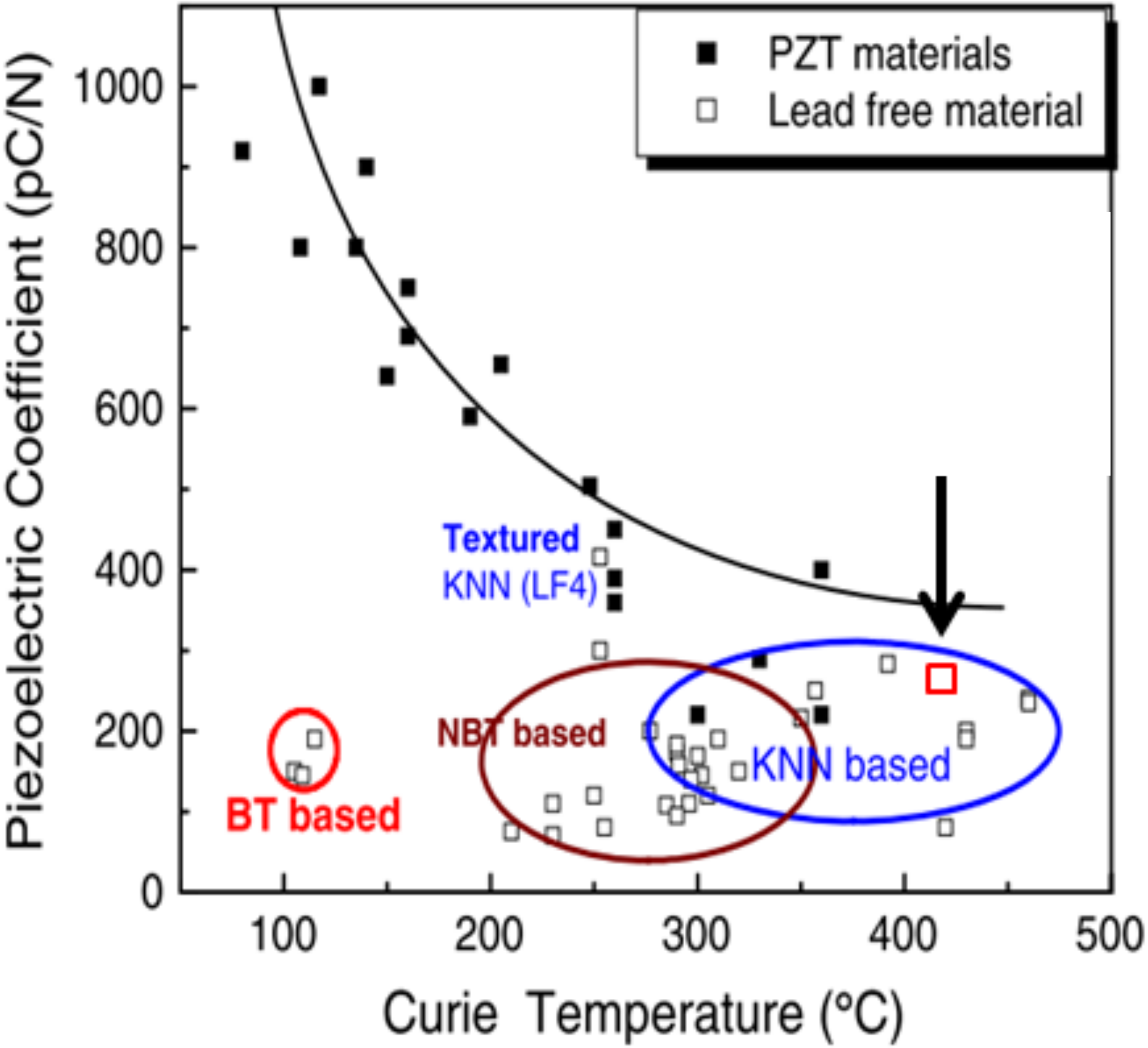
Jaffe, B., W.R. Cook, and H. Jaffe, *Piezoelectric ceramics*. Vol. 3. 1971: AcadEmic Press, London

$(K_{0.5}Na_{0.5})NbO_3$



Jing-Feng Lu, et al, J. Am. Ceram. Soc. 96, 12, 3696, 2013

Benchmarking



Piezoelectric Materials

Material	Dielectric constant	Dielectric loss	d_{33} (pC/N)	k_p	k_{33}	T_C (˚C)	Ref.
$(K_{0.5}Na_{0.5})NbO_3$ (Hot-Pressed)	500	0.2	127	0.46	0.6	420	[1, 2]
$(K_{0.5}Na_{0.5})NbO_3$	290	0.4	80	0.35	0.51	420	[3]
KNN-LF4 (textured)	1570		410	0.61		253	[4]
PZT (Type Navy I)	1250	0.4	290	0.59	0.72	325	[5]
Morgan type 402 Hard Piezoceramic	1200	0.003	285	0.56	0.70	320	[6]
PZT (Type VI) Soft Piezoceramic	3400	1.70	650	0.77		180	[5]

1.R. E. Jaeger and L. Egerton, J. Am. Ceram. Soc. 45, 209-213 (1962)
2.G. H. Haertling, J. Am. Ceram. Soc. 50, 329-330 (1967)
3.L. Egerton and D. M. Dillon, J. Am. Ceram. Soc. 42, 438-442 (1959)
4.Y. Saito, et al, Nature, 432, 84-87 (2004).
5.http://www.americanpiezo.com/apc-materials/piezoelectric-properties.html retrieved on 28-06-2011
6.http://www.morganelectroceramics.com/materials/piezoelectric/ retrieved on 28-06-2011

$NaNbO_3$ – $KNbO_3$

- **1951** — Early work on $KNbO_3$ and $NaNbO_3$
- **1954** — Properties of KNN by Shirane *et. al*
  Phys Rev 96(3):581–588, 1954
- **1960** — Work focused on PZT, BT
  Structural, microstructural, electromechanical characterization
  Wide applications BT / PZT
- **1990** — Environmental awareness, focus on Pb-free
- **2004** — Ground breaking work of Saito *et. al.*
  Nature 432, 84-87, 2004
- **2011** — Research focused on maximizing electromechanical response of KNN
- Transferring lead-free piezoelectrics into application
  Roedel et al, J. Eur. Ceram. Soc., 2015
- **2015** — Thick KNN films by EPD
  Vilarinho et al, RSC Adv ., 2015
- Thick KNN films byAqueous EPD
  Vilarinho et al, Langmuir, 2016

- There is a need …
- Our approach
- Our results
- What I´ve just said …

Aqueous based EPD of KNN

Materials preparation

Preparation KNN powders

- XRD
- Thermal Analysis

Preparation KNN aqueous suspensions

- UV transmitance
- Zeta potential

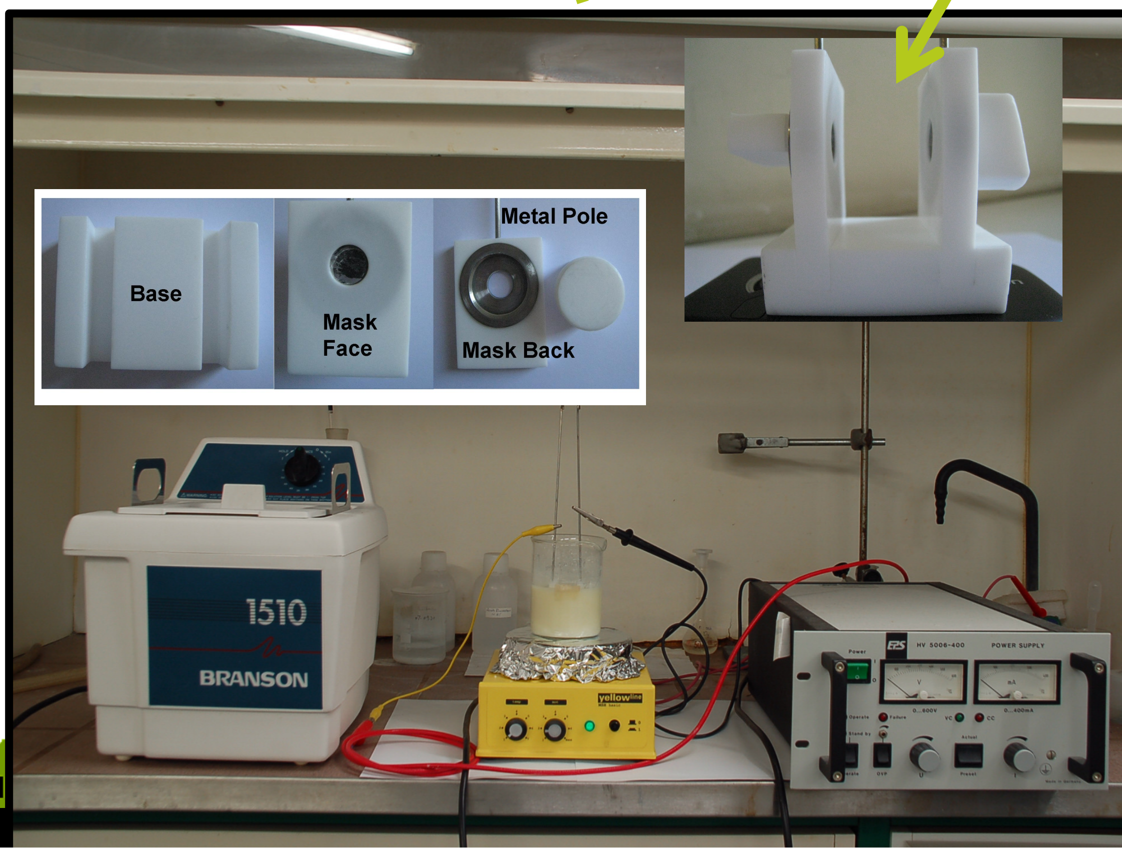
EPD

- potencial
- time

Densification

Isostatic Pressing (200 Mpa/2h)
Sintering (1100ºC/2h

- Densiy
- SEM
- Dielectric measurements



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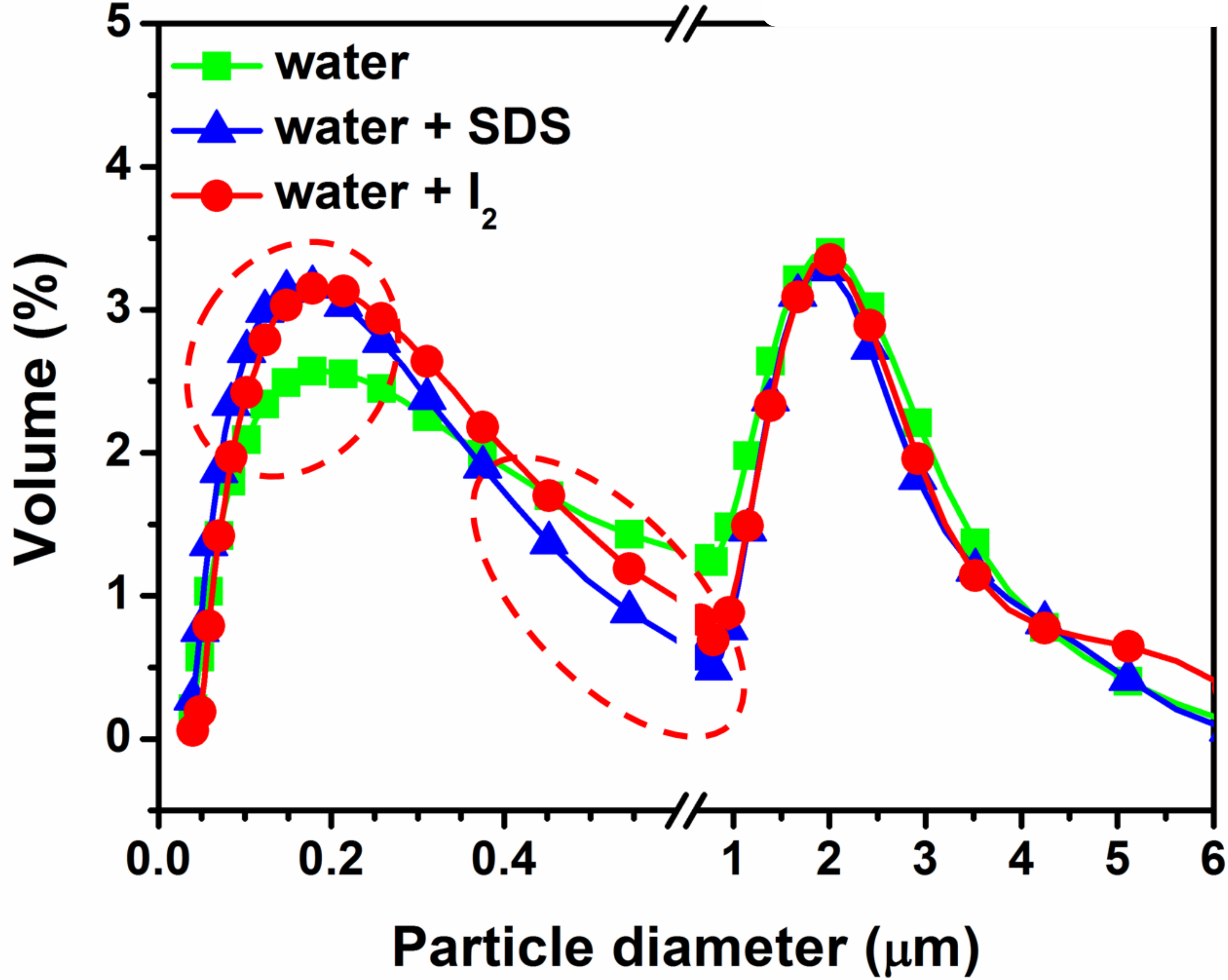
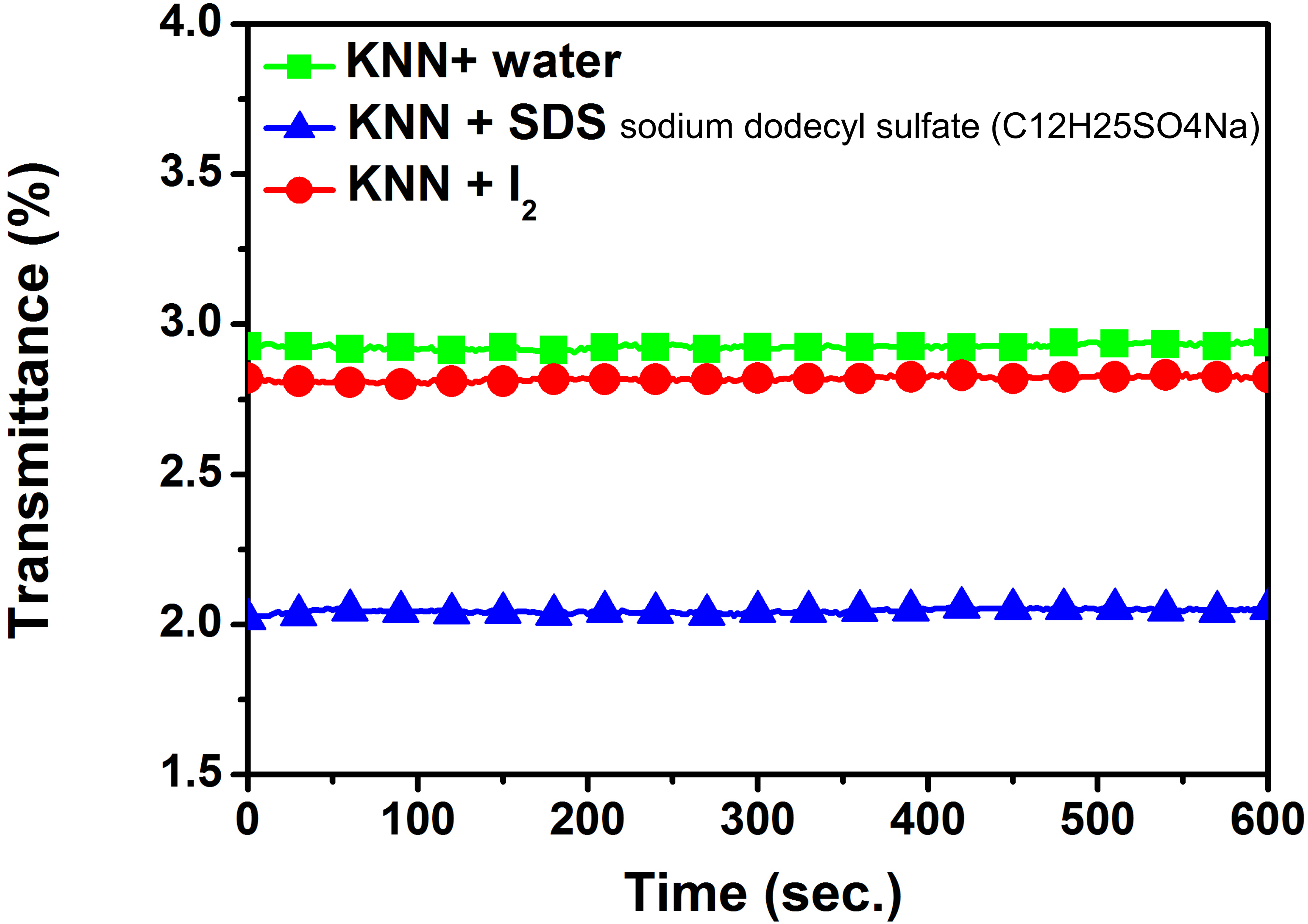
Powders and suspension characterization

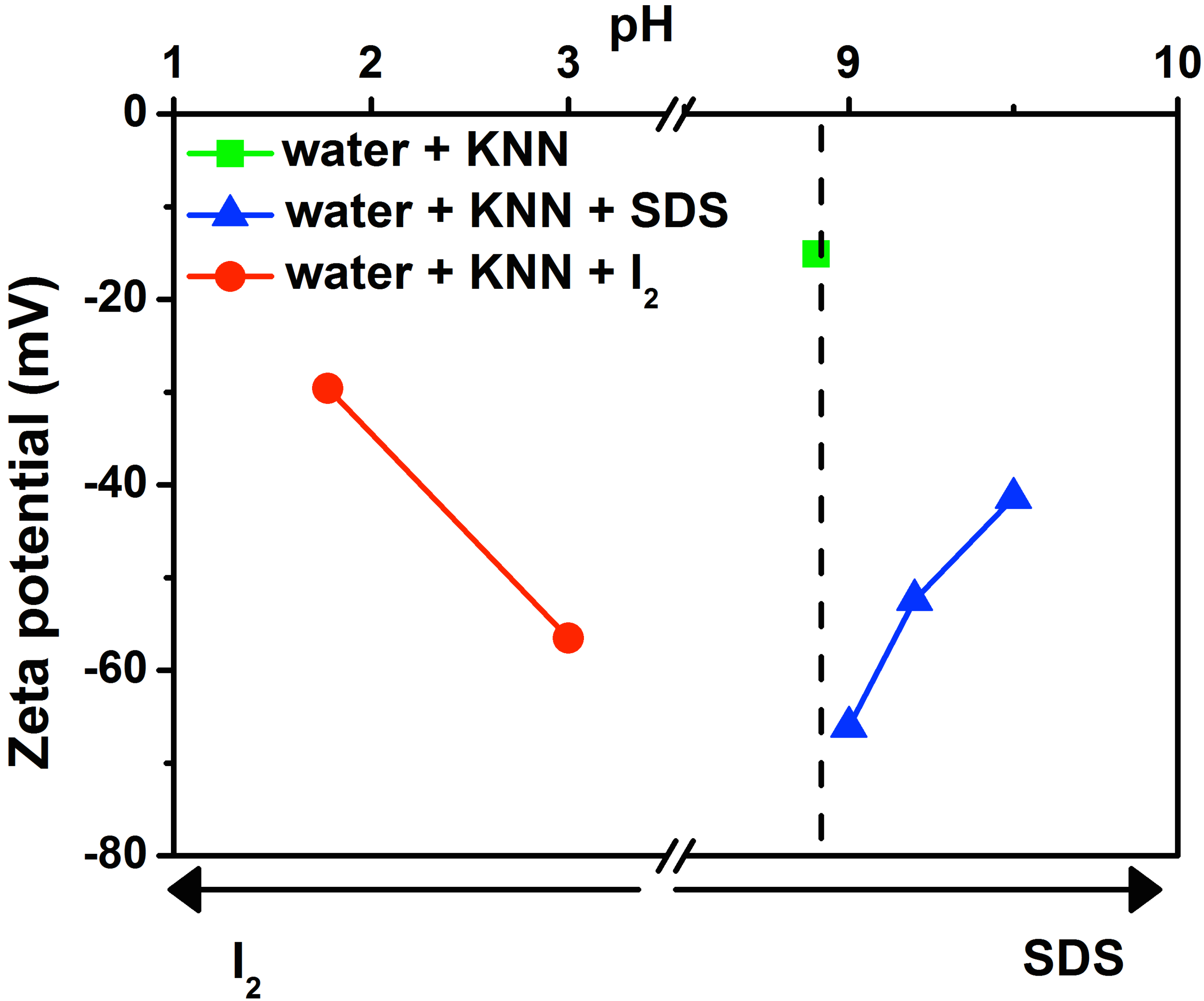
Suspension characterization



Suspension characterization



Suspension characterization

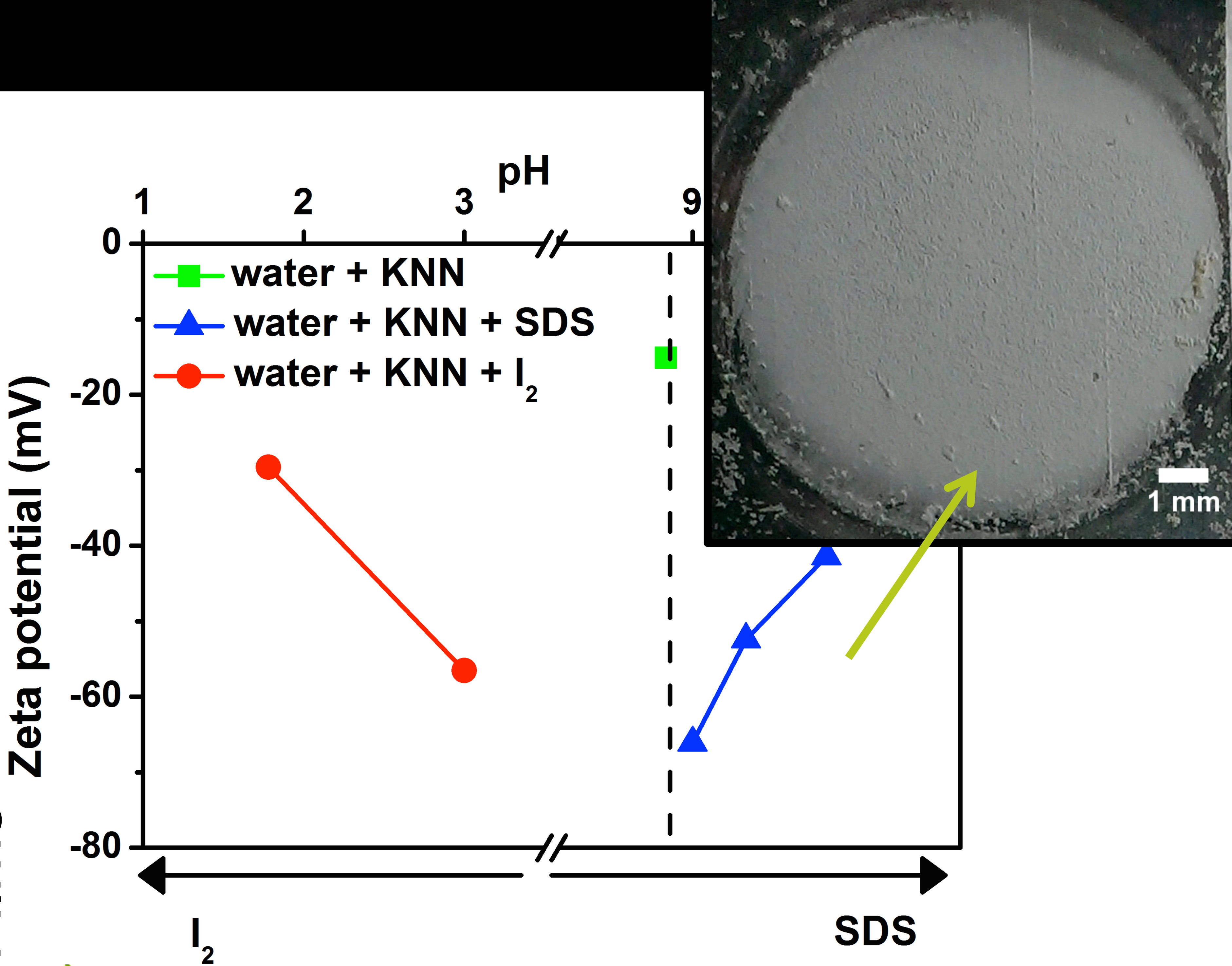


Suspension media	Zeta potential (mV)	pH	Deposition Electrode	Film quality
Water	-15.1	8.9	Anode	Poor
Water + SDS (0.02 : 100 wt. ratio of SDS solution in KNN suspension)	-76.9	8.7	Anode	Uniform
Water + iodine (0.02 : 100 wt. ratio of iodine solution in KNN suspension)	-56.7	3	Anode	Very poor

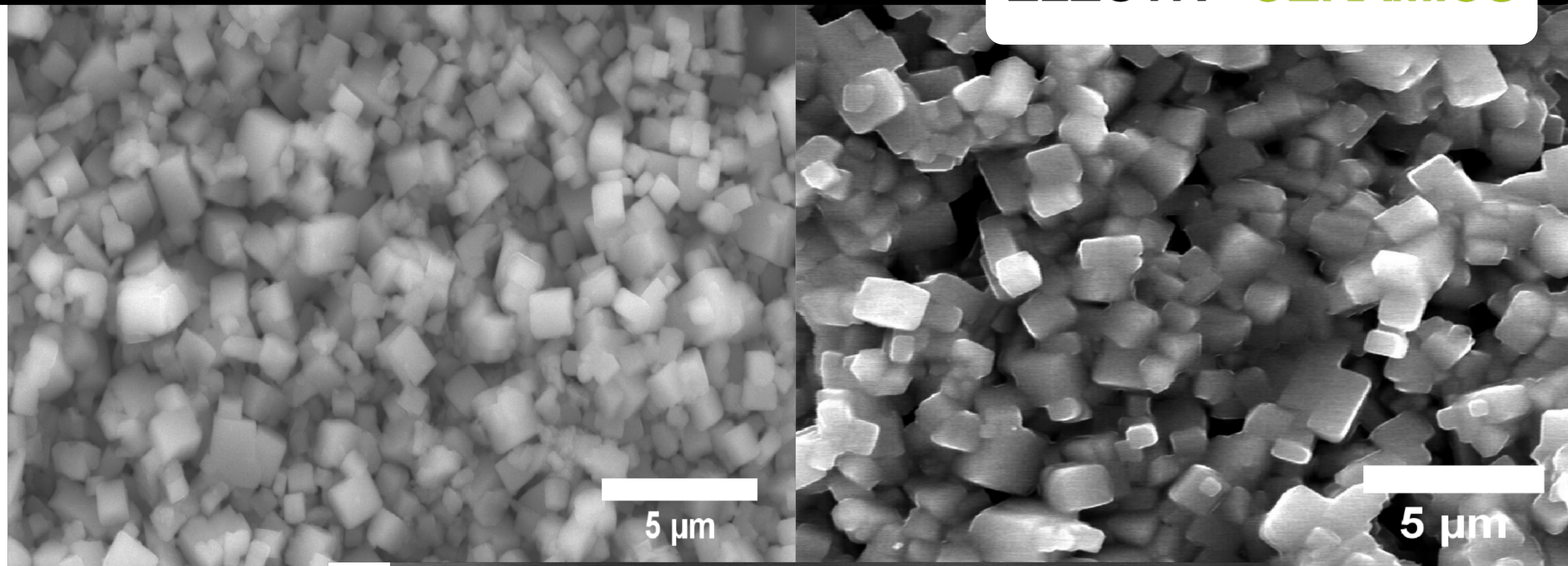
Summary of aqueous suspension parameters such as pH and zeta potential for which $K_{0.5}Na_{0.5}NbO_3$ thick films were obtained with the application of 10 V for 20 min.

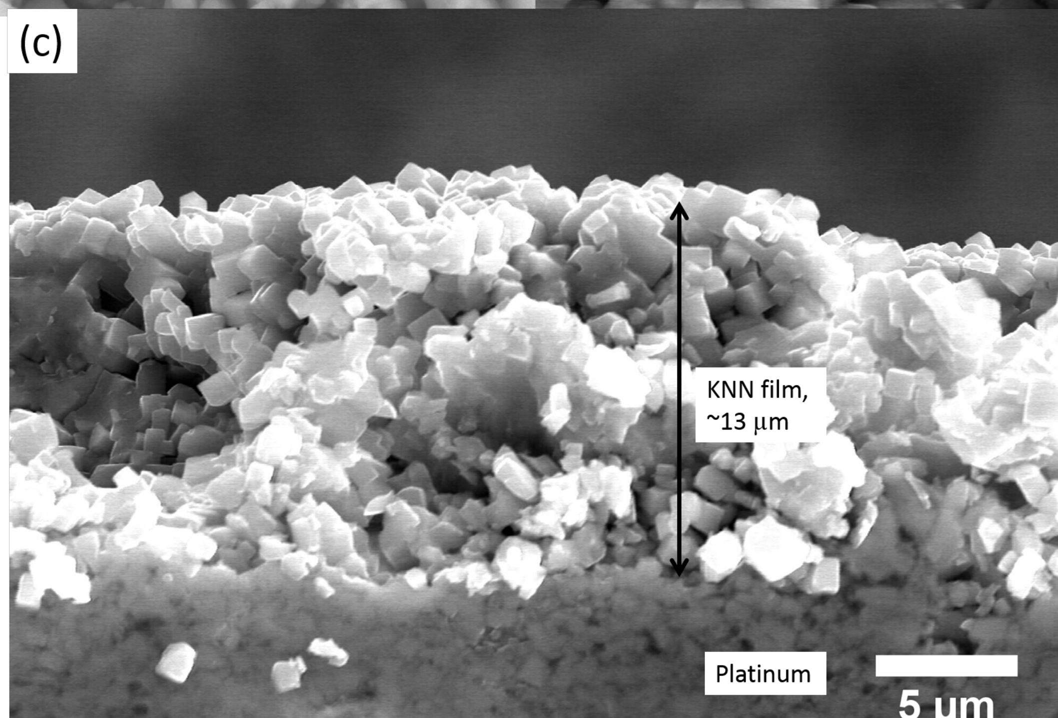
Films characterization

Films

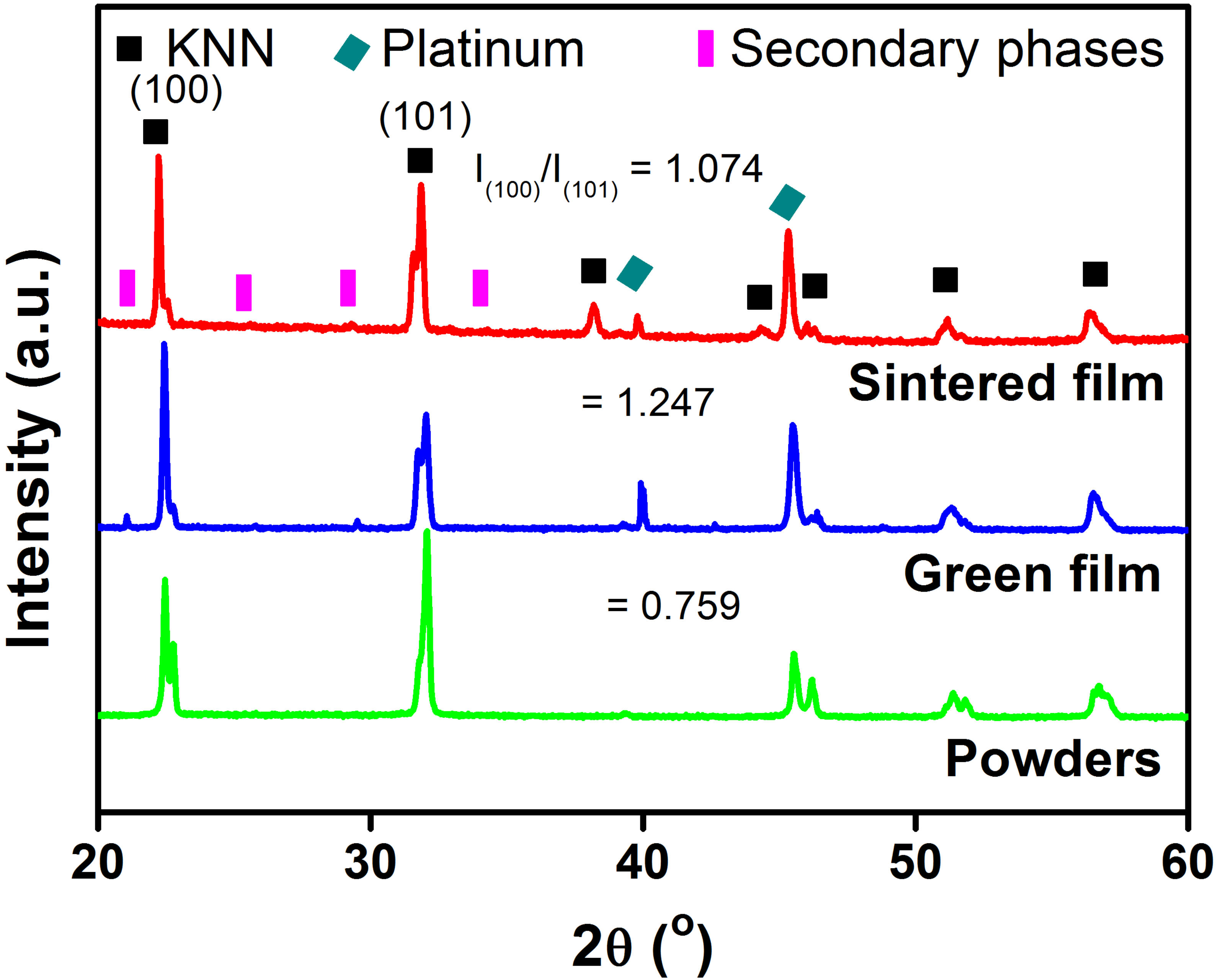

pH
1
2
3
9
0
-20
-40
-60
-80
Zeta potential (mV)
water + KNN
water + KNN + SDS
water + KNN + I_2
1 mm
I_2
SDS

Films characterization

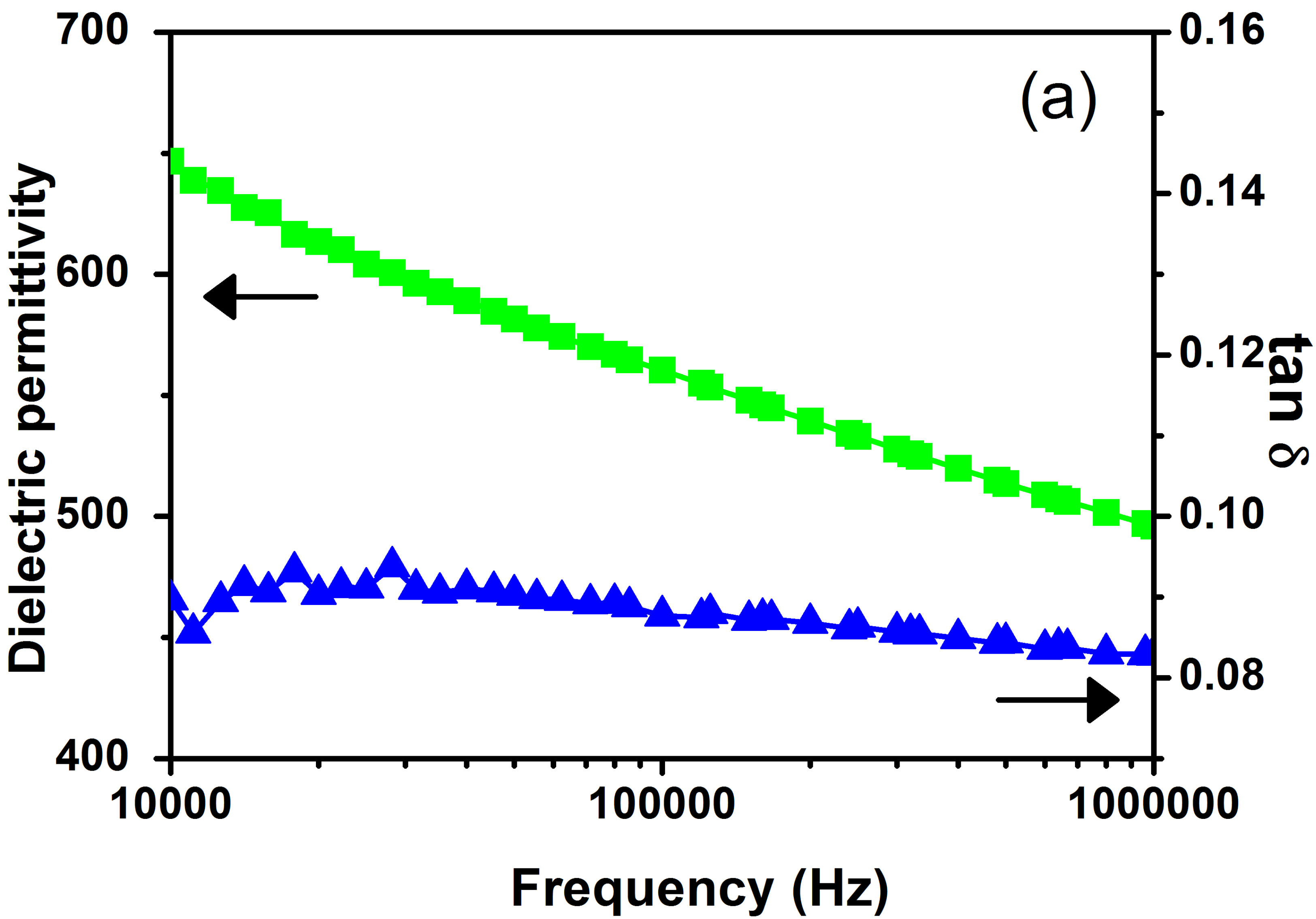




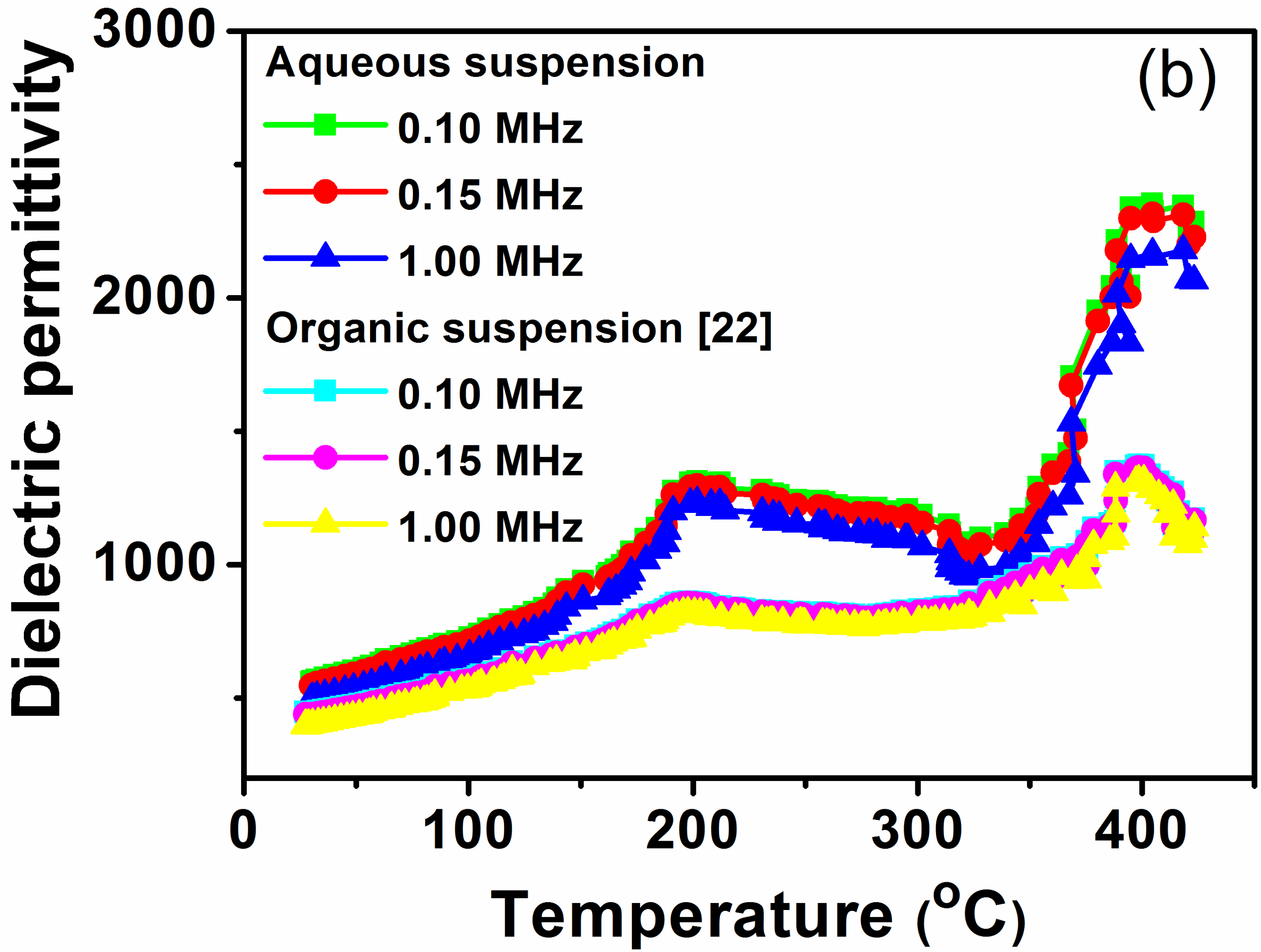
Films characterization



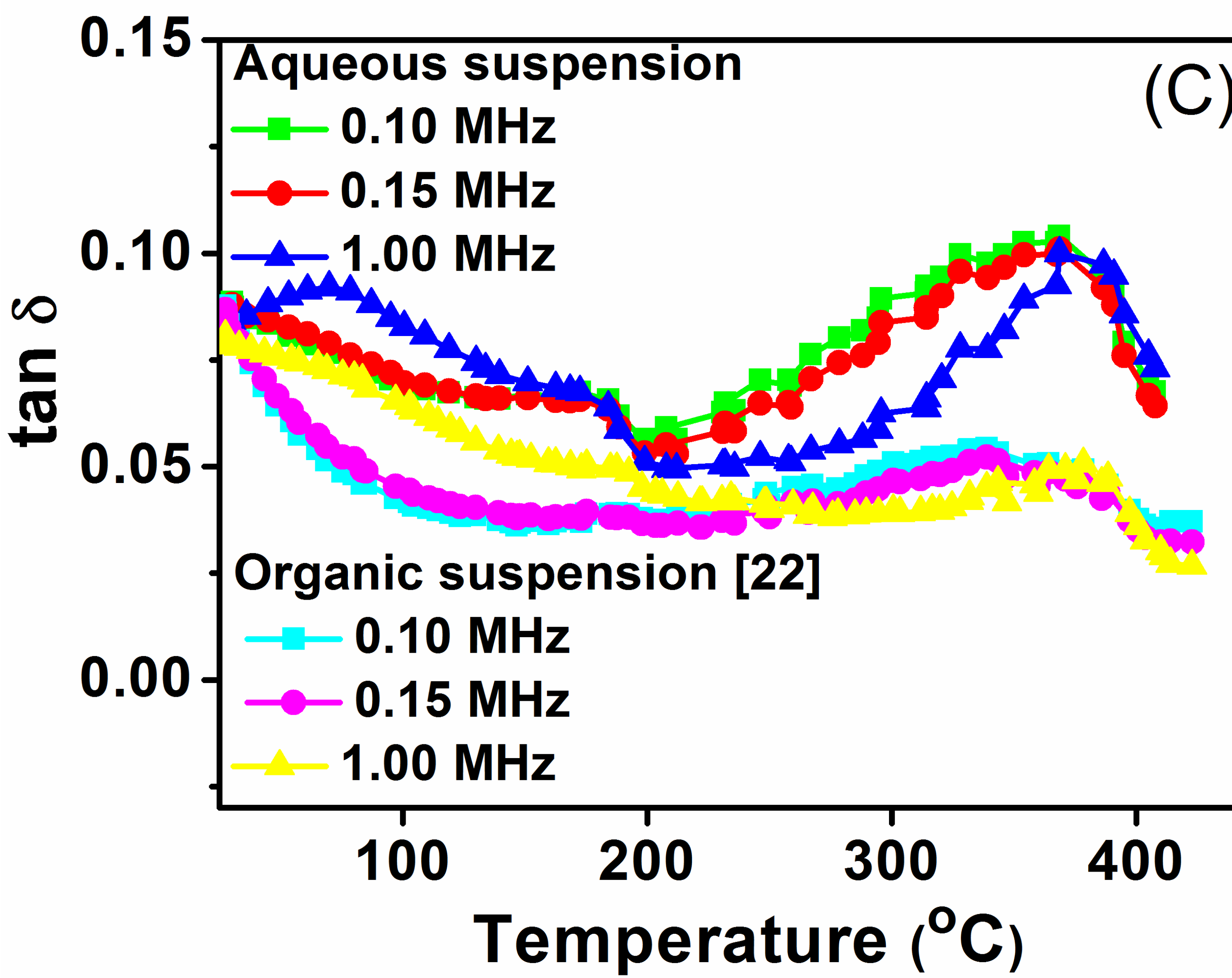
Films characterization



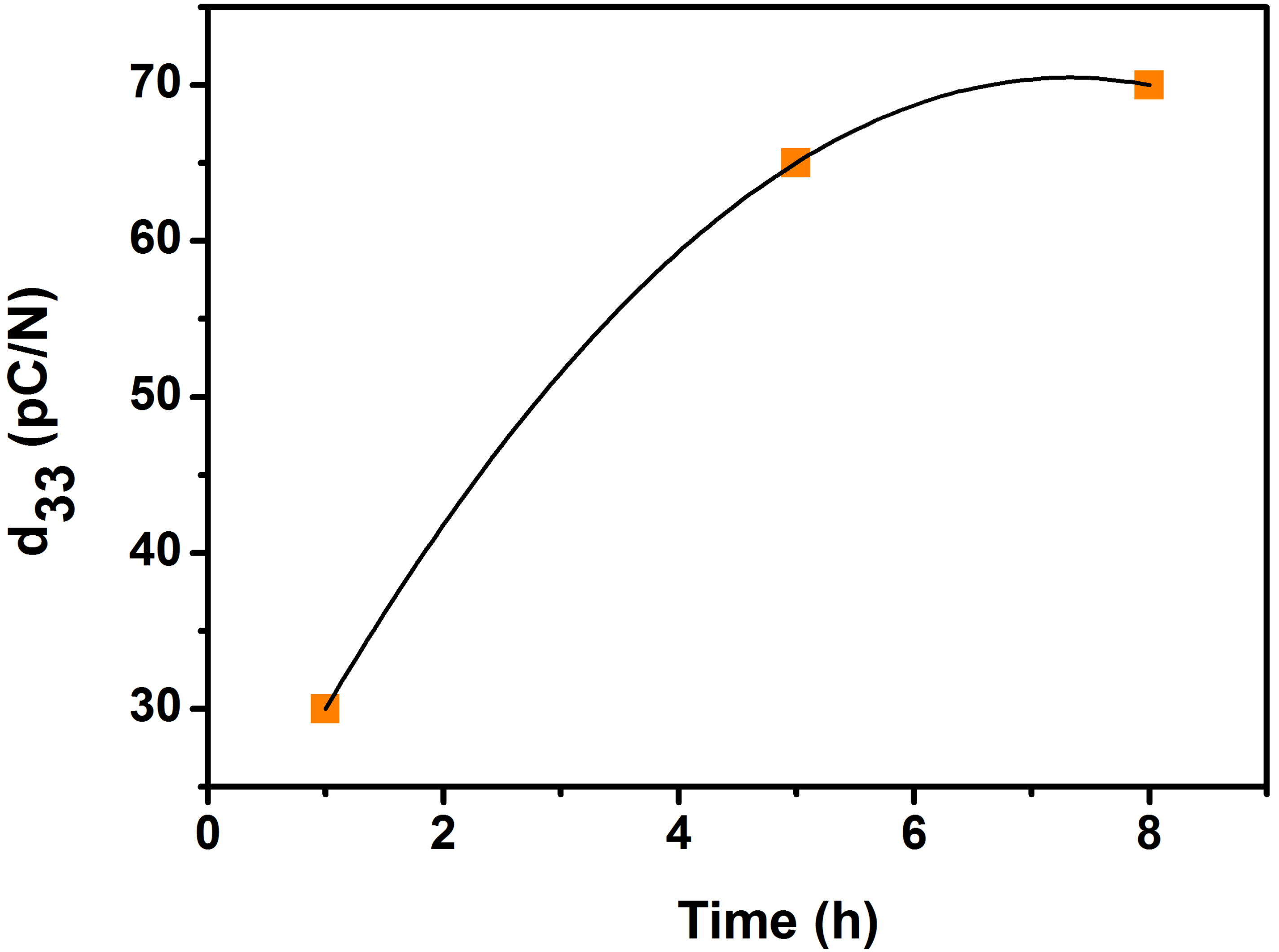
Films characterization



Films characterization



Films characterization



Films characterization

Material	ε_r (T_{room})	T_c (°C)	tanδ	d_{33} (pC/N)	Reference
KNN (1:1) thick films by EPD using aqueous suspension	495 (1 MHz)	404	0.08 (1MHz)	68	Present work
KNN (1:1) thick films by EPD using organic suspension	392 (1 MHz)	400	0.07 (1MHz)	40	22
KNN thick films by sol gel	250 (1 KHz)		1.3	18	48
KNN thick films by aerosol deposition	116 (as-deposited) 545 (annealed) (1 kHz)		0.04		51
KNN (1:1) ceramics	290 (1 kHz)	420	0.04 (1 kHz)	80	41
KNN (1:1) hot pressed ceramics	420 (1 kHz)			160	43
$(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.84}Ta_{0.10}Sb_{0.06})O_3$ ceramic (LF4T) textured ceramics	1570 (1 kHz)	253		410	7
KNN (1:1) single crystals [001]	300 (1 kHz)	429		160	52
KNN (1:1) single crystals [001]	240 (100 kHz)	393	0.02 (100 kHz)	160	50
KNN (1:1) single crystals [131]	1015 (100 kHz)	410	0.01 (100 kHz)	50	53
KNN (1:1) single crystals [323]	650 (100 kHz)	409	0.01 (100 kHz)	-	53

Dielectric and piezoelectric coefficient d_{33} data for $K_{0.5}Na_{0.5}NbO_3$ (KNN) single crystals, ceramics and thick films of this work and previously reported.

Our contribution

LANGMUIR

Article

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Unleashing the Full Sustainable Potential of Thick Films of Lead-Free Potassium Sodium Niobate ($K_{0.5}Na_{0.5}NbO_3$) by Aqueous Electrophoretic Deposition

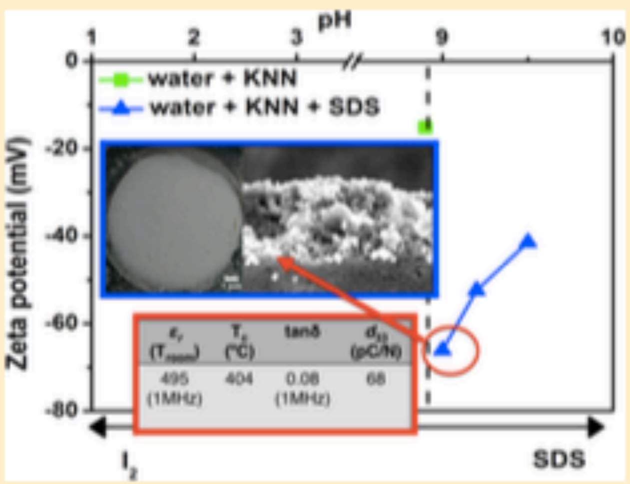
Amit Mahajan,[†,‡] Rui Pinho,[†] Morgane Dolhen,[†,§] M. Elisabete Costa,[†] and Paula M. Vilarinho*[,†]

[†]Department of Materials and Ceramic Engineering, CICECO, Aveiro Institute of Materials, University of Aveiro, 3810-193 Aveiro, Portugal

[§]Science of Ceramic Processing and Surface Treatments, University of Limoges, 87060 Limoges, France

Supporting Information

ABSTRACT: A current challenge for the fabrication of functional oxide-based devices is related with the need of environmental and sustainable materials and processes. By considering both lead-free ferroelectrics of potassium sodium niobate ($K_{0.5}Na_{0.5}NbO_3$, KNN) and aqueous-based electrophoretic deposition here we demonstrate that an eco-friendly aqueous solution-based process can be used to produce KNN thick coatings with improved electromechanical performance. KNN thick films on platinum substrates with thickness varying between 10 and 15 μm have a dielectric permittivity of 495, dielectric losses of 0.08 at 1 MHz, and a piezoelectric coefficient d_{33} of ~70 pC/N. At T_C these films display a relative permittivity of 2166 and loss tangent of 0.11 at 1 MHz. A comparison of the physical properties between these films and their bulk ceramics counterparts demonstrates the impact of the aqueous-based electrophoretic deposition (EPD) technique for the preparation of lead-free ferroelectric thick films. This opens the door to the possible development of high-performance, lead-free piezoelectric thick films by a sustainable low-cost process, expanding the applicability of lead-free piezoelectrics.



- There is a need …
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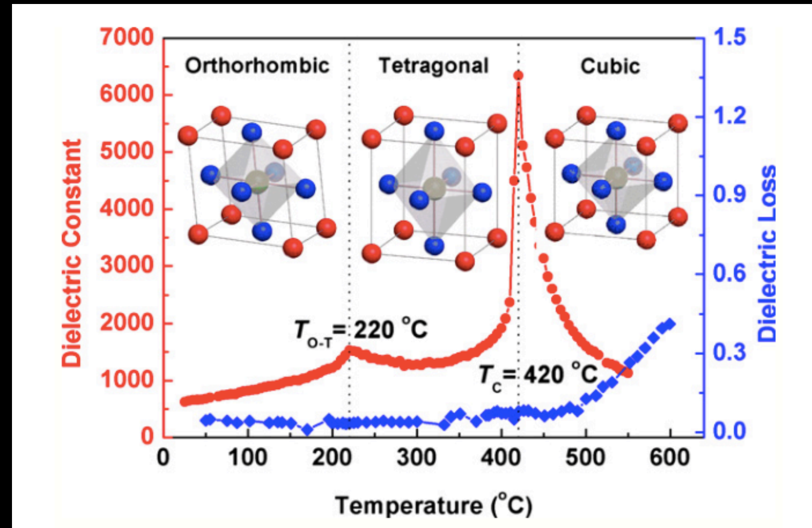
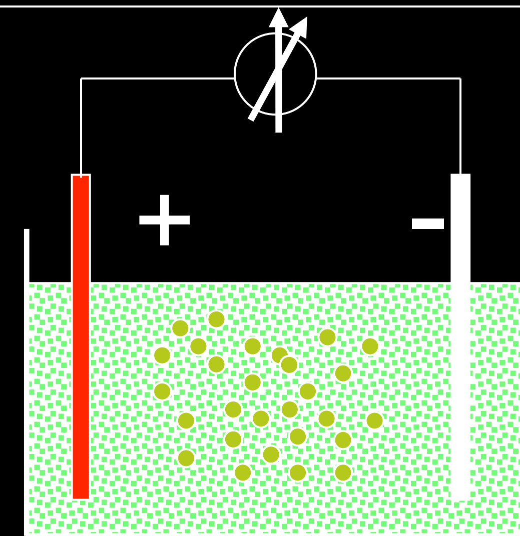
Sustainabilty

Lead Free Piezos

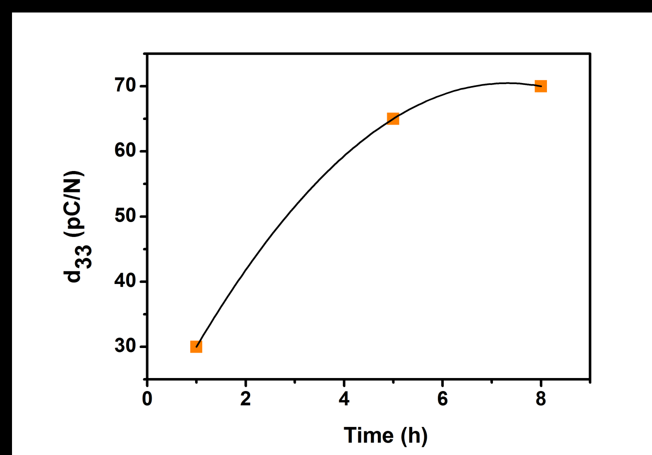


Miniaturization



Aqueous EPD

Sustainable piezoelectrics



Sustainable wearables

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ELECTROCERAMICS

ACKNOWLEDGMENTS

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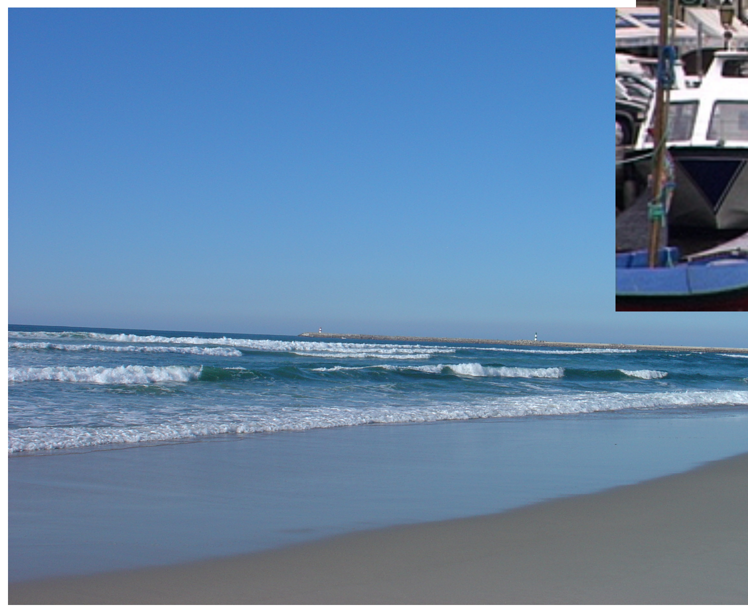
cost



Thanks for your attention

관심을 가져 주셔서 감사합니다.

ANNOUNCEMENTS

PORTUGAL // The Beauty of Simplicity

https://www.youtube.com/watch?v=kXsQif3QLjs#t=175