GREMAN
matériaux microélectronique
acoustique nanotechnologies

CENTRE D'ETUDES
ET DE RECHERCHES
TECHNOLOGIQUES EN
MICROELECTRONIQUE
(CERTeM)

Séminaire Scientifique CERTeM 2020

Nouveau banc de polarisation et caractérisation de propriétés piézoélectriques

cnrs
advancing the frontiers

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TOURS

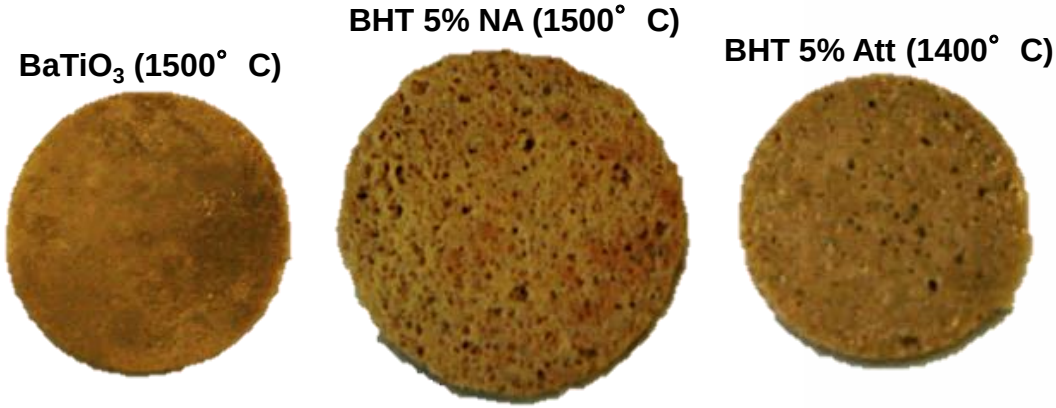
Jeudi 29 septembre 2016

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Collaboration avec CEA Le Ripault (thèse T. Richardot)

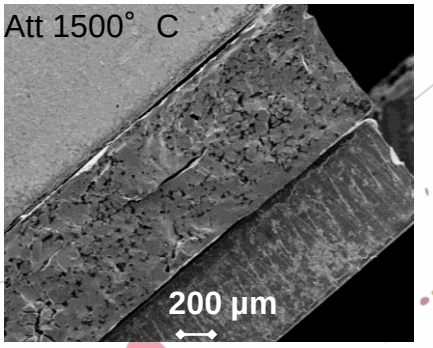
Céramiques massives sans plomb (BHT)



➔ **Optimisation des conditions de polarisation nécessaire**
(Champ électrique, température, temps….)

➔ **Mesures des propriétés après l'étape de polarisation (mesures d'impédance électrique ou Berlincourt-mètre (d_{33})**

Echantillon	BHT 5% Att	BHT 7,5% Att	BHT 10% Att	BHT 5% Att
$T°_{frittage}$ (° C)	1400	1400	1400	1500
$\varepsilon_{33}^S/\varepsilon_0$	655	740	790	695
k_t (%)	31	31	34	45
δm (%)	20	32	21	11
δe (%)	1	1	1	3

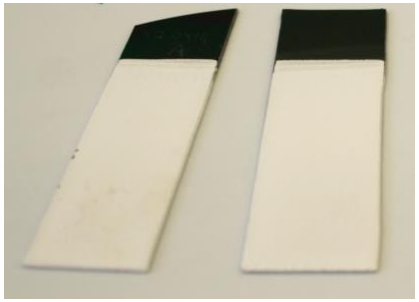


Collaboration avec CEA Le Ripault (thèse T. Richardot)

Films épais sans plomb (BHT)

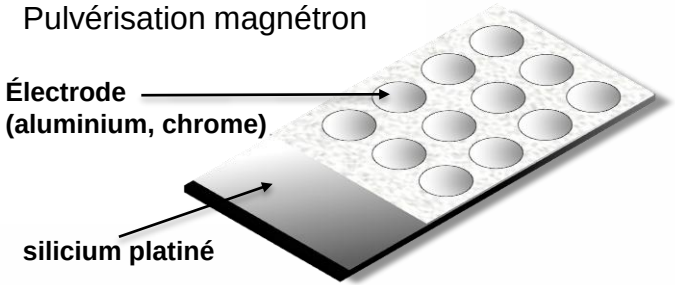


1-Trempage-retrait sur substrat de silicium

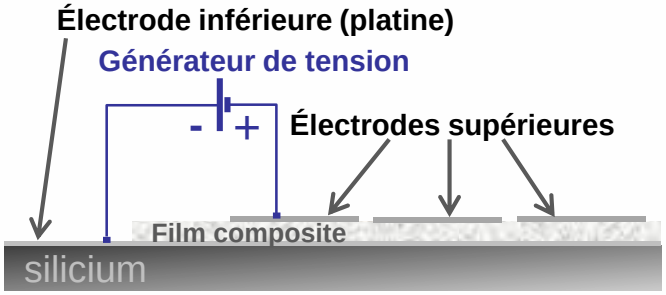


2-Dépôt des électrodes supérieures

Pulvérisation magnétron



3-Polarisation (field cooling)



4-Mesure d'impédance



➔ **Optimisation des conditions de polarisation nécessaire**

Collaboration avec l'IJS et VERMON (thèse en co-tutelle H. Mercier)

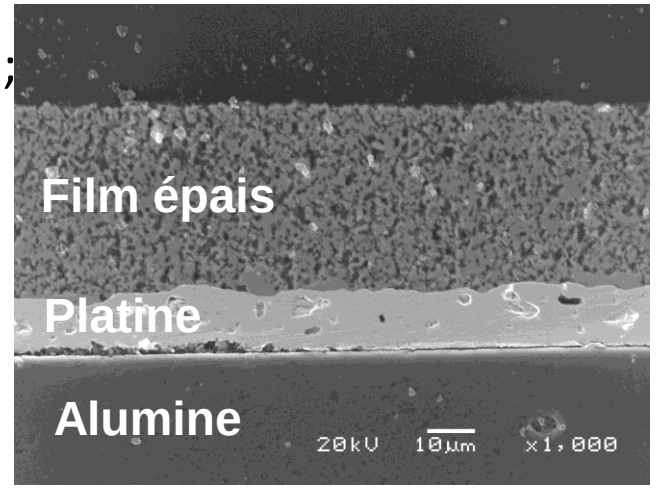
Institut "Jožef Stefan" Ljubljana, Slovenija

vermon
world leader in Composite Piezoelectric Transducers

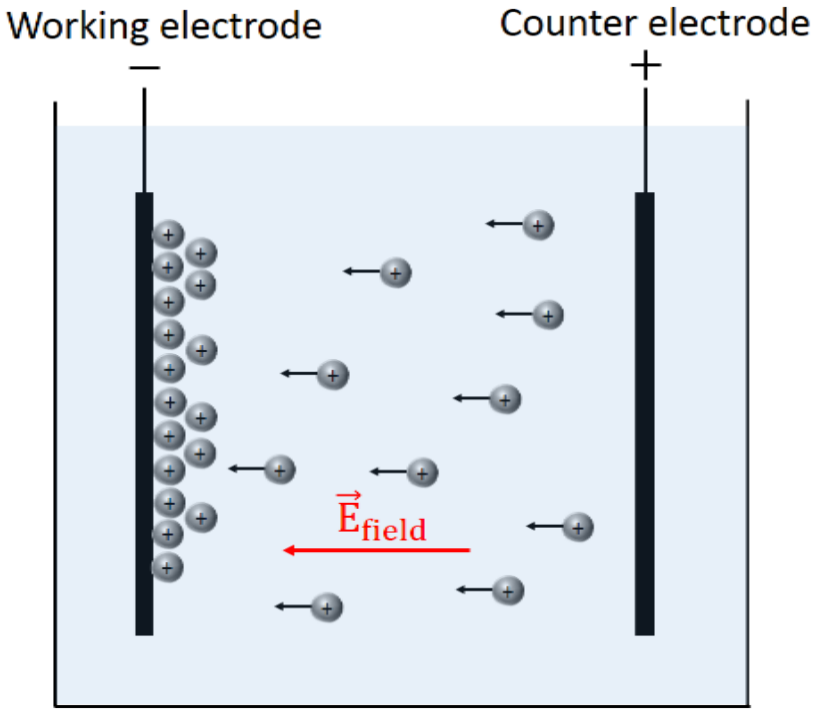
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Films épais sans plomb (KNNSr – Electrophorèse)

- Déposition sur des substrats de formes complexes;
- Dépôt de films épais (plusieurs dizaines de microns);
- Méthode peu couteuse.



Fritté à 1100° C, 2h dans l'air



Pour l'électrophorèse :

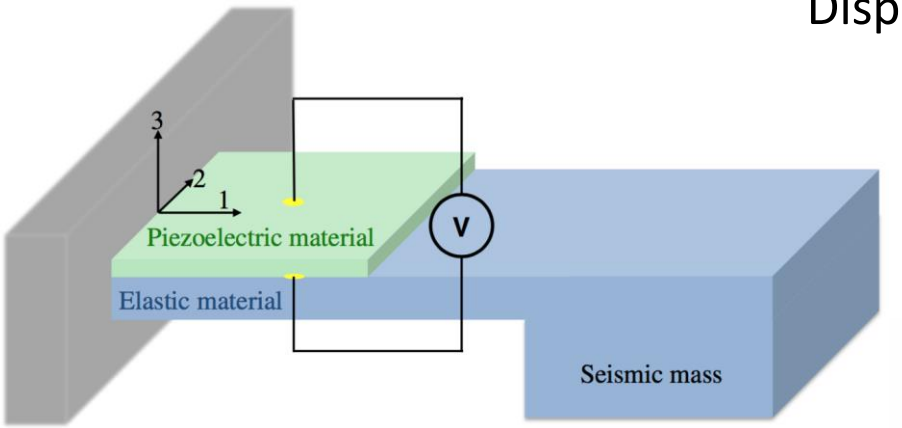
- Suspension stable et les particules bien dispersées;
- Faible conductivité.

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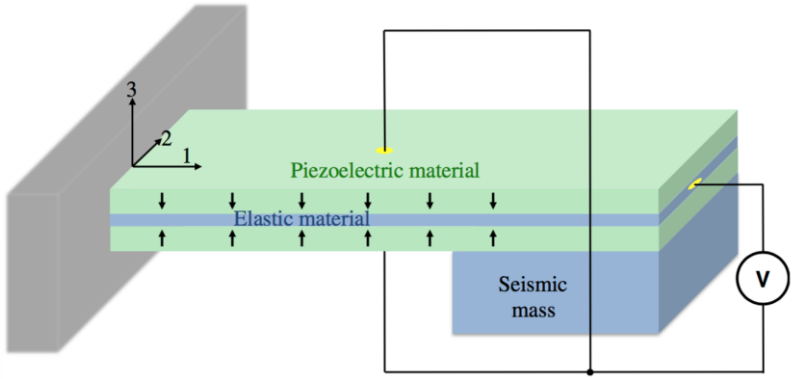
Collaboration avec l'IJS et VERMON (thèse en co-tutelle H. Mercier)

Récupération d'énergie

Dispositifs



"Unimorph Configuration"



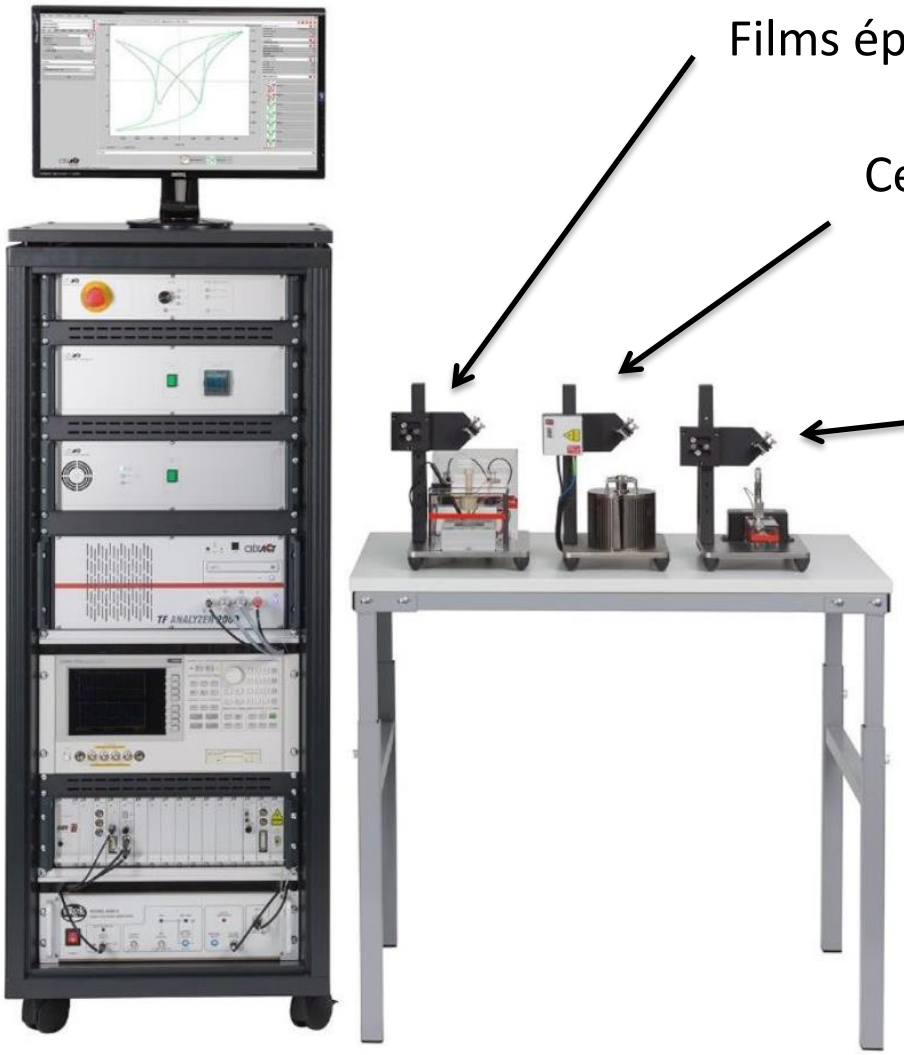
"Bimorph configuration"

Figure de mérite pour le matériau piézoélectrique : $FOM_{mat} = e^2_{31,f}/(\varepsilon_0 \varepsilon_{33})$

➔ **Mesure du coefficient $e_{31,f}$ indispensable**

Banc de caractérisation

Piezoelectric evaluation system (PES)



Films épais (et mesure $e_{31,f}$)

Céramique massive

Films fins (et mesure $e_{31,f}$)

Dispositif modulable

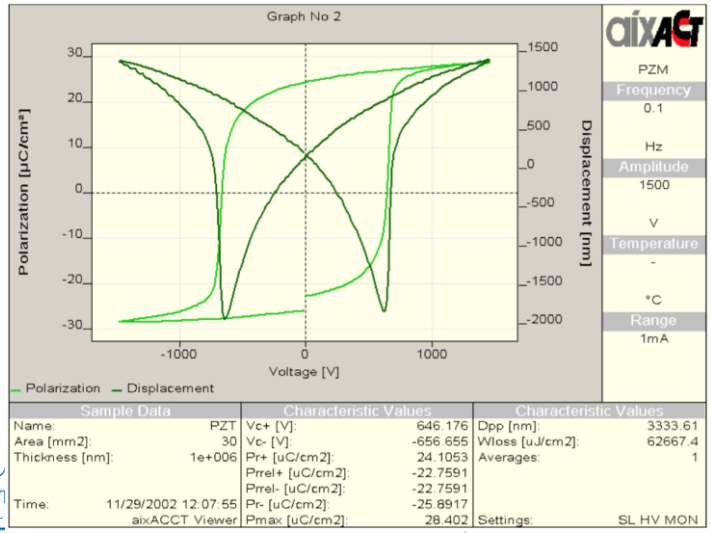
Banc de caractérisation

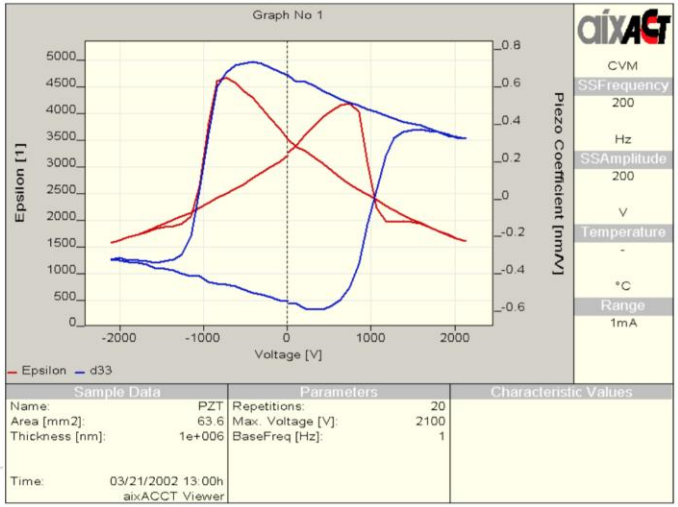
aixPES



Céramiques massives

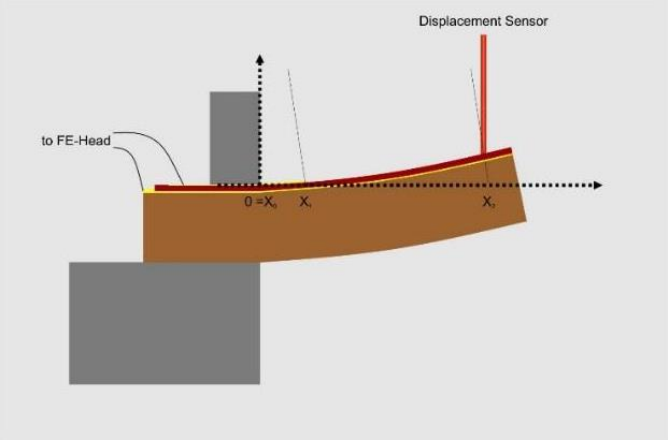
- Tension maximale applicable +/-4000 V
- Utilisation d'huile silicone possible
- Taille maximale des échantillons (diamètre 26 mm et épaisseur 10 mm)
- température : ambiante à 250° C ;
- mesures C(V), ε, tanδ,d_{33} (petit et grand signaux), P_r^+, P_r^-, V_c^+, V_c^-,



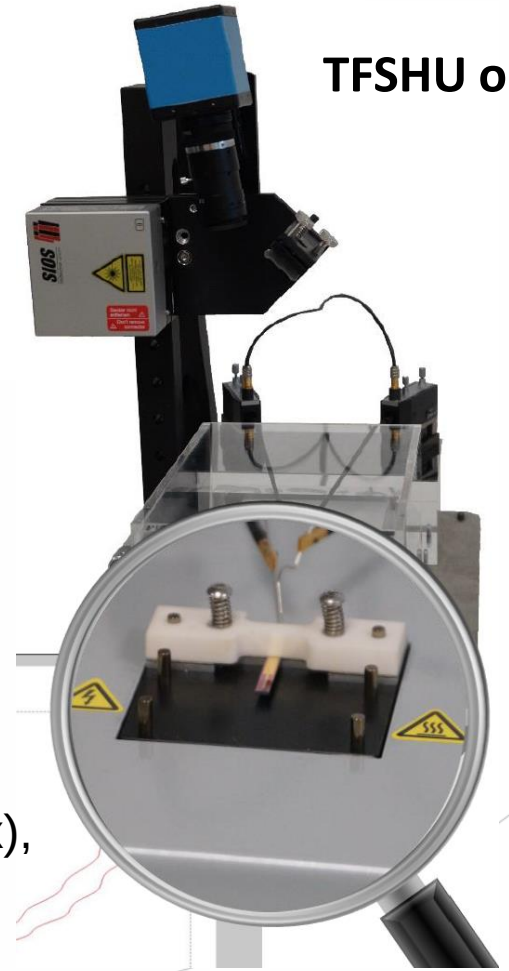


Banc de caractérisation

Films épais et mesures de e31,f (indirect)



TFSHU option



- Tension maximale applicable +/-500 V
- Utilisation d'huile silicone possible
- Cuve de 50mm*50mm
- température : ambiante à 250° C ;
- mesures C(V), ε, tanδ,d_{33} (petit et grand signaux), P_r^+, P_r^-, V_c^+, V_c^-,

Banc de caractérisation

Films épais et mesures de e31,f (indirect)

Relations utilisées:

$$e_{31,f} = \frac{Y_s (h_s)^2}{3(1-\nu_s) L^2} \frac{\delta}{V}$$

h_s : substrate thickness
Y_s : substrate Young's modulus
ν_s : substrate Poisson's ratio
L : cantilever length
V : applied voltage
δ : displacement (measured at L)

Electrode partielle

$$e_{31,f} = \frac{Y_s (h_s)^2}{3(1-\nu_s)} \frac{1}{c_f x_1 (2L - x_1)} \frac{\delta}{V}$$

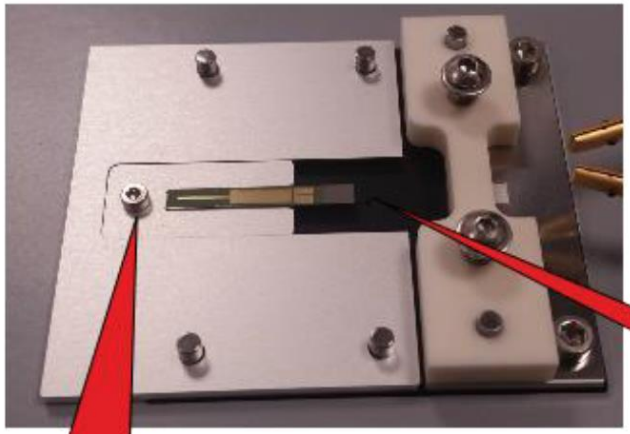
c_f : electrode coverage factor (elect. width/subst. width)
x_1 : electrode length

[1] I. Kanno et al. / Sensors and Actuators A 107 (2003) 68–74
[2] M.-A. Dubois and P. Muralt, Sens. Actuators 77, pp106 (1999)
[3] Chun, D.-M., Sato, M., and Kanno, I., Journal of Applied Physics 113, 044111 (2013)
[4] A. Mazzalai, D. Balma, N. Chidambaram, J. Li, and P. Muralt, P., Proc. of ISAF/PFM, pp363-366, 2013

Banc de caractérisation

Films épais et mesures de e31,f (indirect)

Placement de l'échantillon:



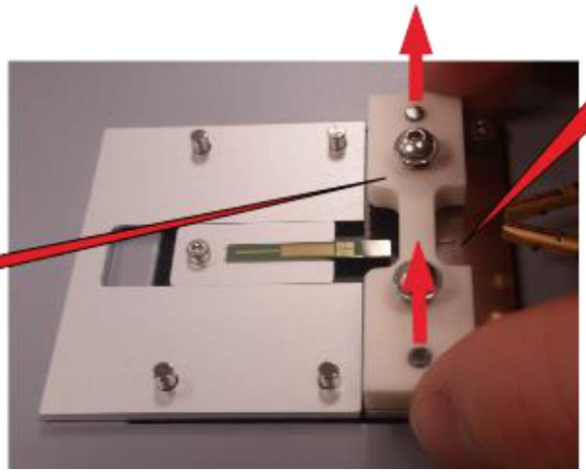
1. Place the sample onto the inserting aid

2. Lift the clamping device and slip the sample through it until it fits the spacing

Sample

Spacing

Inserting aid

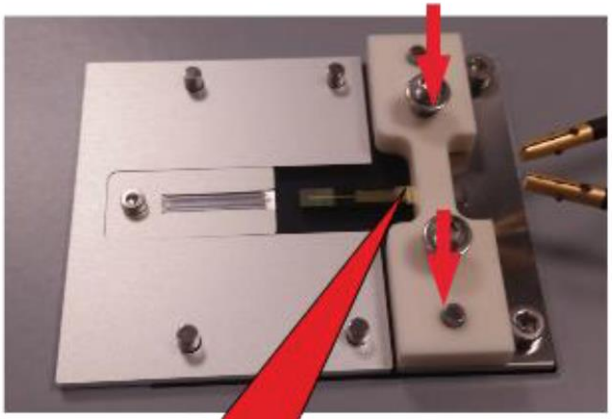


Clamping device

Banc de caractérisation

Films épais et mesures de e31,f (indirect)

Placement de l'échantillon:

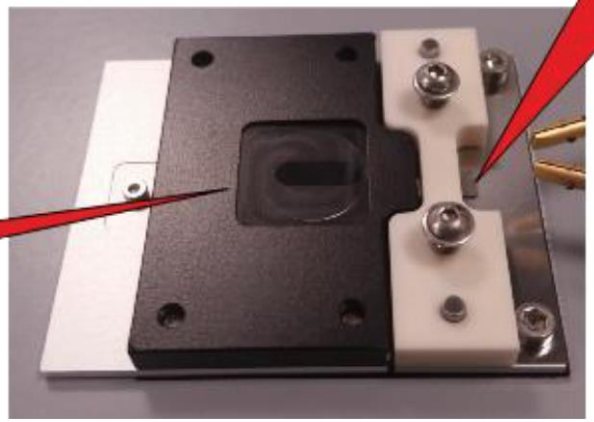


3. Release the clamping device and pull back the inserting aid completely.

4. Place the heating cover and contact the sample using the positioner.

Test sample contacting area

Normal Sample contacting area



Heating cover with glas plate (not for test sample)

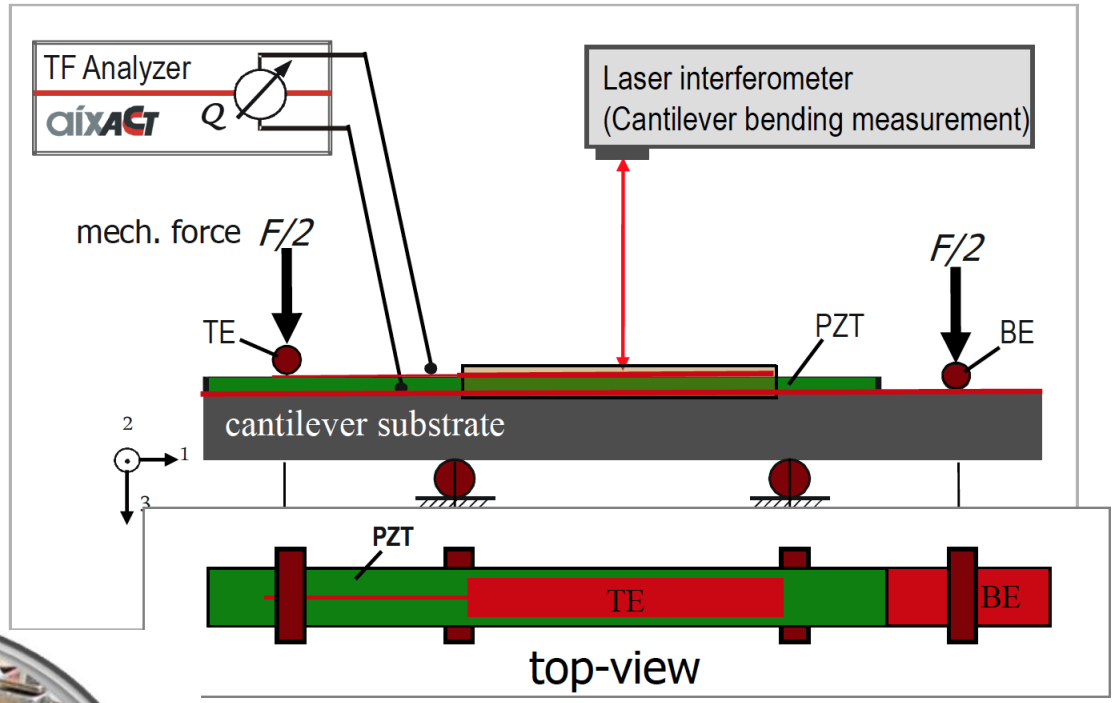
Banc de caractérisation

Films fins et mesures de $e_{31,f}$ (direct)

aix4PB







EPFL, P. Muralt

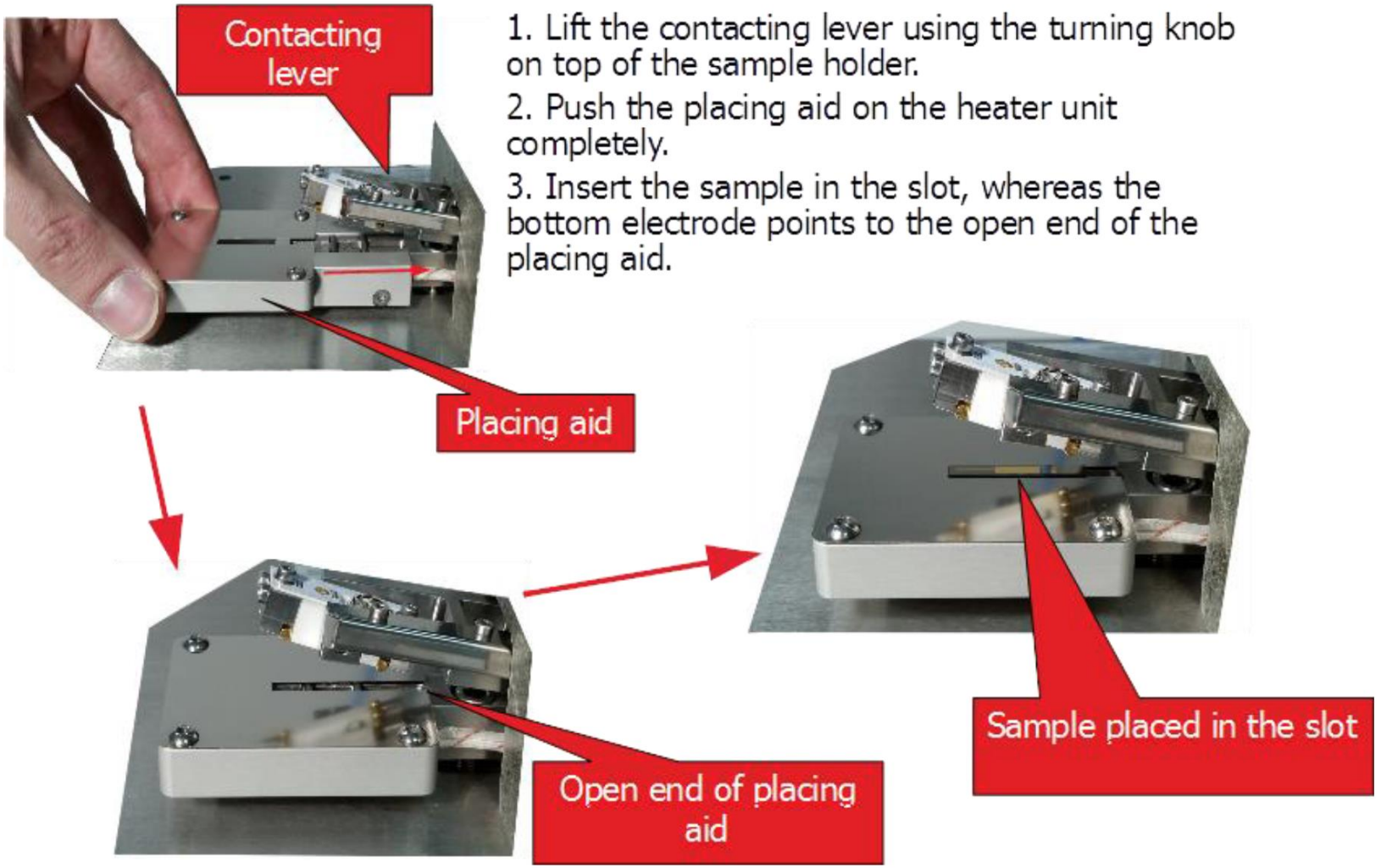
$$|e_{31,f}| = \frac{Q\, l_1^2}{4\, A\, h\, u_{3,cant}\, (1 - \nu_{Substrate})}$$

Patent pending (2005):
German Patent and Trade Mark Office,
Akz 10 2005 006 958.4

Banc de caractérisation

Films fins et mesures de $e_{31,f}$ (direct)

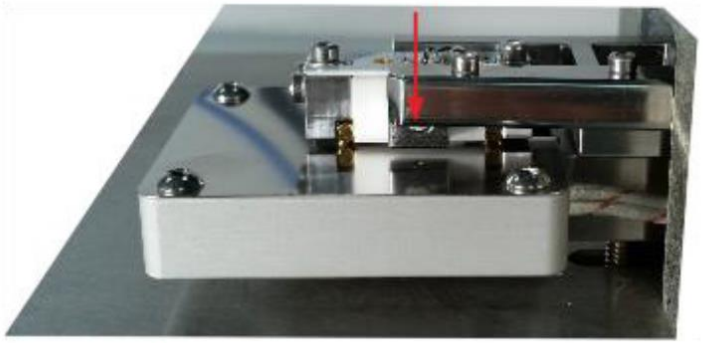
Placement de l'échantillon:



Banc de caractérisation

Films fins et mesures de $e_{31,f}$ (direct)

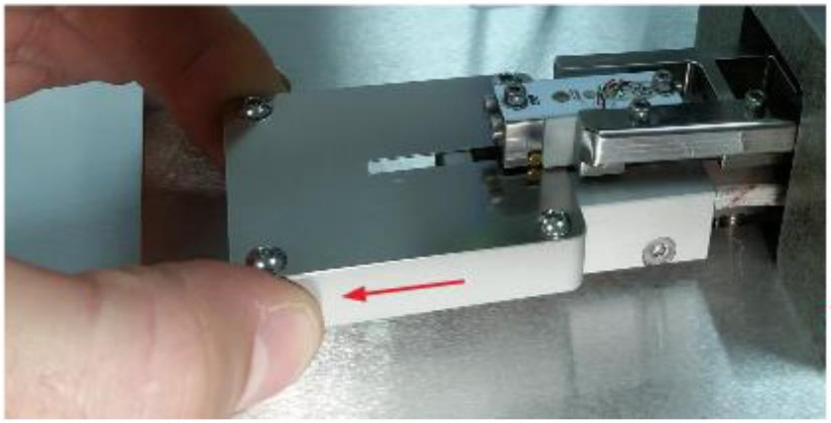
Placement de l'échantillon:



4. Lower the contacting lever using the turning knob on top of the sample holder, until it hits the sample

Be careful. The sample could break, if there is too much force on it.

5. Pull out the placing aid on the heater unit completely





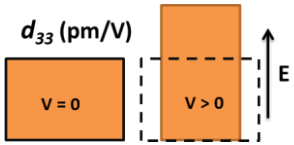
Banc de caractérisation

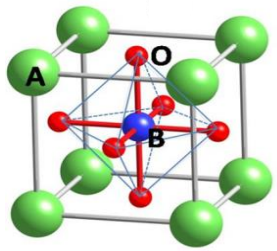
Films fins, mesures de d_{33} et cycles de polarisation

Piezoelectricity and materials

Most used material for MEMs applications : $PbZr_{1-x}Ti_xO_3$

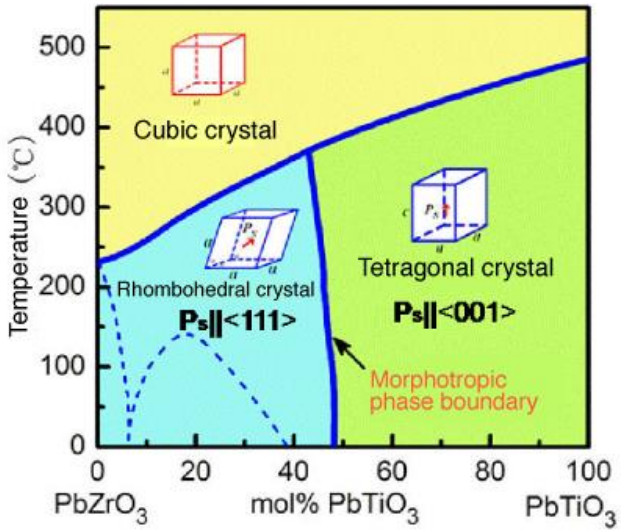
- High piezoelectric coefficients
- High electromechanical coupling

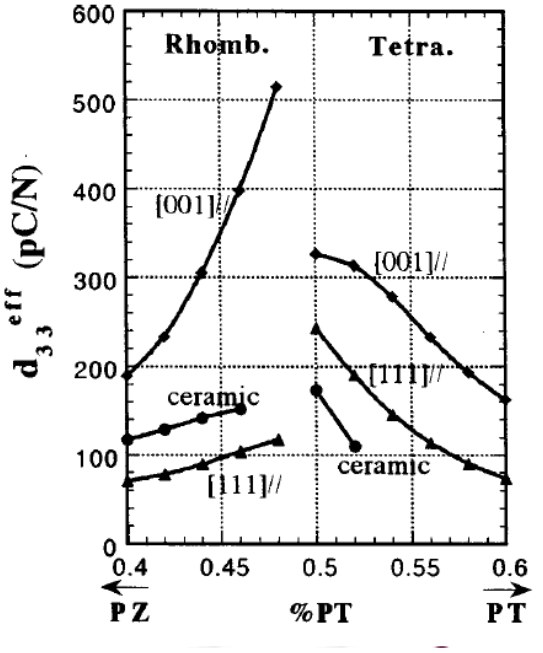




Perovskite ABO_3

PZT phase diagram



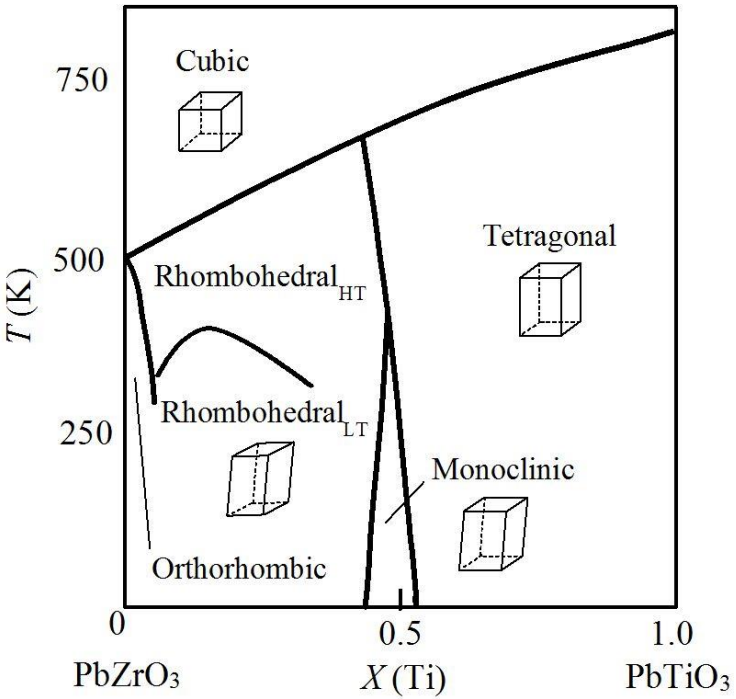


Du *et al.* Appl. Phys. Lett., Vol. 72, No. 19, 11 May 1998

Enhanced properties at MPB
due to coexistence of R and T (60's)

Piezoelectricity and materials

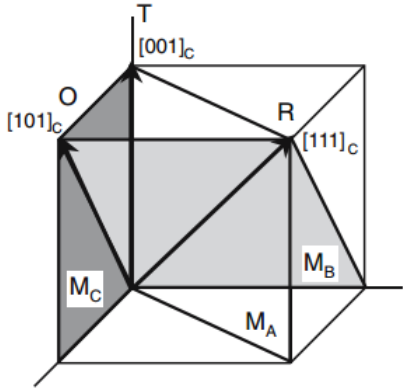
MPBs revisited in late 1990's early 2000's



Existence of monoclinic phases at the MPB

Structural bridge between R and T phases

Polarization rotation *during* R ➔ M ➔ T transitions
key for giant piezoelectric coefficients



Universal mechanism for giant piezoelectric coefficients materials

Relaxors-ferroelectrics PMN–xPT and PZN–xPT
($(1–x)Pb(Mg_{1/3}Nb_{2/3})O_3–xPbTiO_3$ and $(1–x)Pb(Zn_{1/3}Nb_{2/3})O_3–xPbTiO_3$)

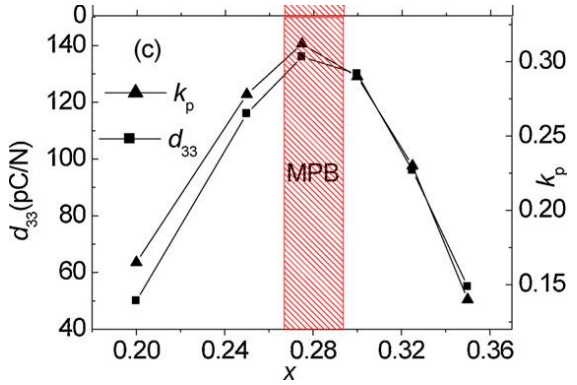
Problem : they are all Pb-based and about to be banned by European regulations

Our goal : Looking for other MPBs in lead-free solid solutions

2 starting point where MPBs already observed:

- **$BiFeO_3$ (rhombo.)**

$(1-x)BiFeO_3 + xPbTiO_3$ (tetra.)



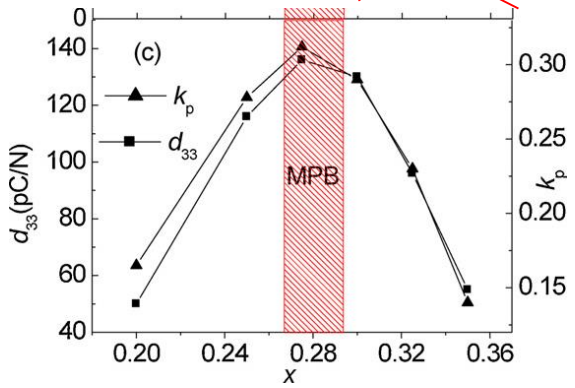
Yang et al, Materials Research Bulletin 47 (2012) 4233–4239

Our goal : Looking for other MPBs in lead-free solid solutions

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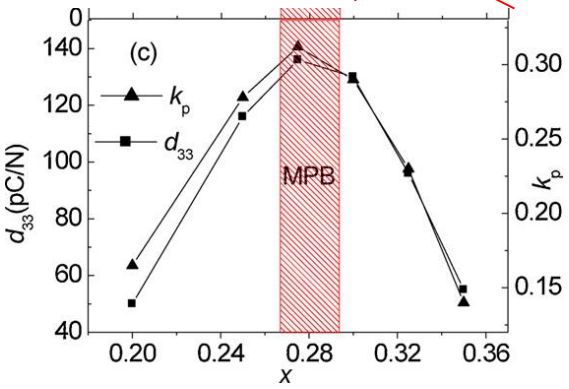
Yang et al, Materials Research Bulletin 47 (2012) 4233–4239

Our goal : Looking for other MPBs in lead-free solid solutions

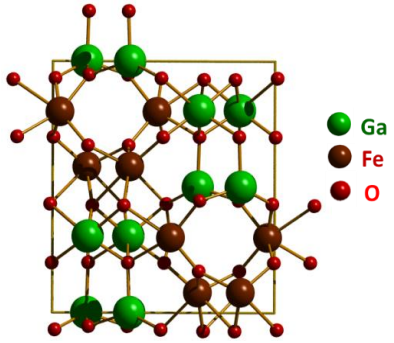
2 starting point where MPBs already observed:

- **$BiFeO_3$ (rhombo.)** + **$GaFeO_3$ (tetra.)**

(1-x)$BiFeO_3$+ x$PbTiO_3$



Yang et al, Materials Research Bulletin 47 (2012) 4233–4239



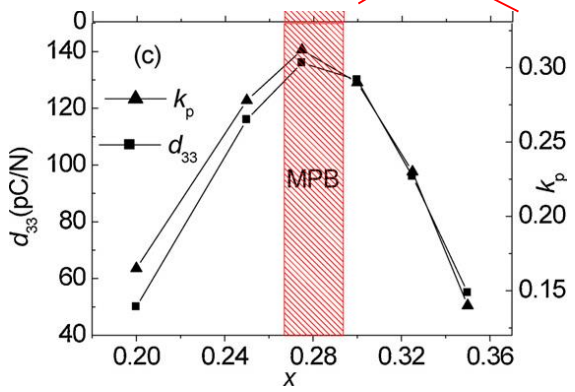
=> (1-x)$BiFeO_3$+ x$GaFeO_3$ = BGFO(x)

Our goal : Looking for other MPBs in lead-free solid solutions

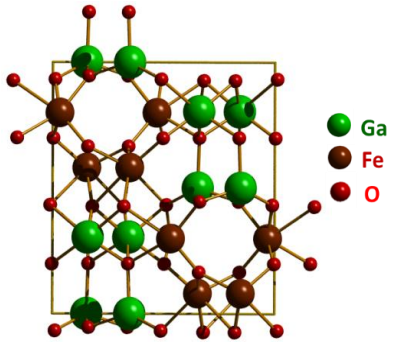
2 starting point where MPBs already observed:

- **$BiFeO_3$ (rhombo.)** + **GaFeO3 (tetra.)**

(1-x)$BiFeO_3$+ x~~$PbTiO_3$~~

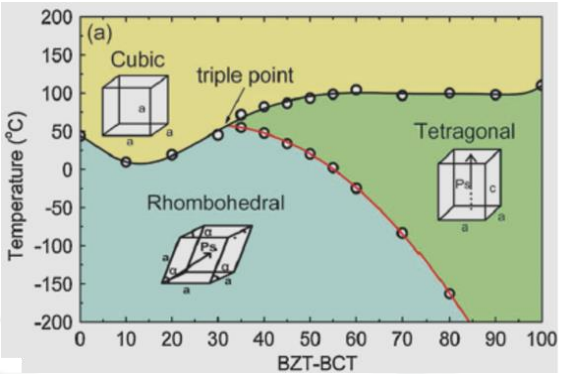


Yang et al, Materials Research Bulletin 47 (2012) 4233–4239



=> (1-x)$BiFeO_3$+ x$GaFeO_3$ = BGFO(x)

- **(1-x) [$BaZr_{0,2}Ti_{0,8}O_3$]-x [$Ba_{0,7}Ca_{0,3}TiO_3$]**



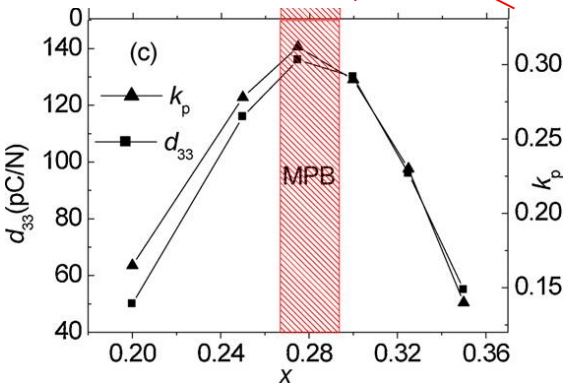
W. Liu et al, PRL 103 (2009) 257602

Our goal : Looking for other MPBs in lead-free solid solutions

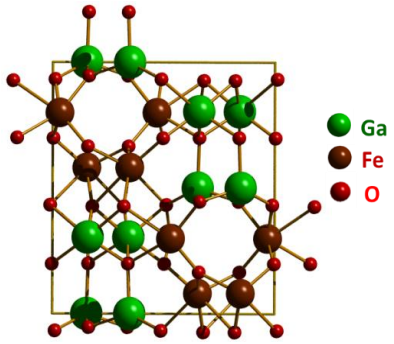
2 starting point where MPBs already observed:

- **$BiFeO_3$ (rhombo.)** + **GaFeO3 (tetra.)**

$(1-x)BiFeO_3+ xPbTiO_3$

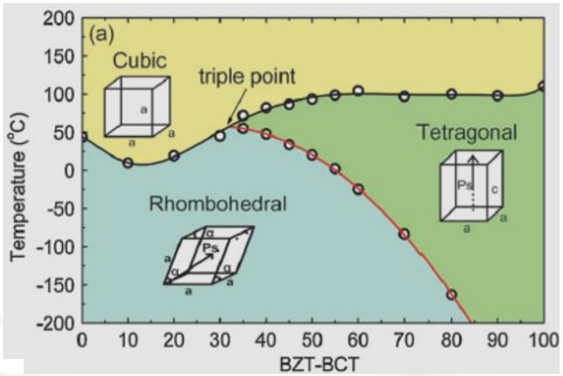


Yang et al, Materials Research Bulletin 47 (2012) 4233–4239

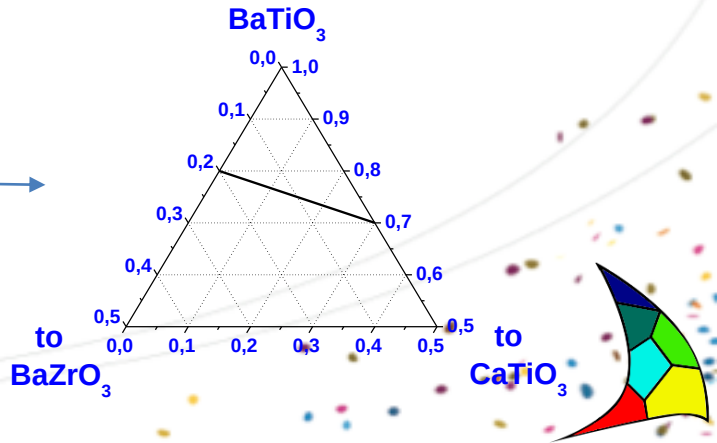


=> $(1-x)BiFeO_3+ xGaFeO_3$ = BGFO(x)

- **$(1-x)\ [BaZr_{0,2}Ti_{0,8}O_3]-x\ [Ba_{0,7}Ca_{0,3}TiO_3]$** **$BaTiO_3$-$BaZrO_3$-$CaTiO_3$ (BCTZ)**



W. Liu et al, PRL 103 (2009) 257602

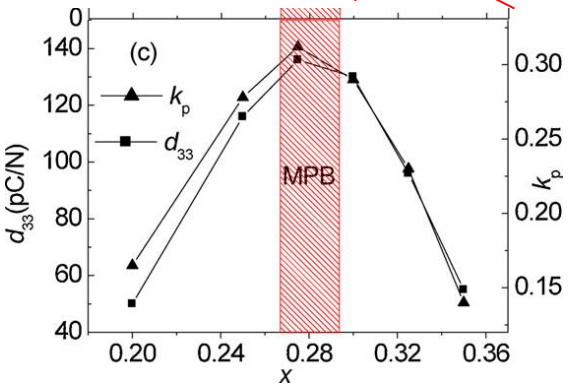


Our goal : Looking for other MPBs in lead-free solid solutions

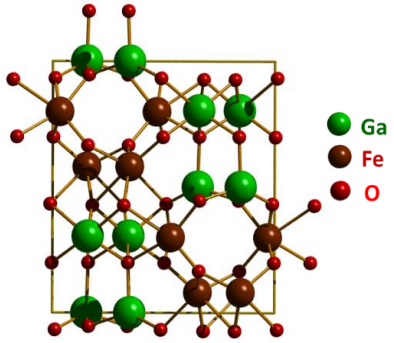
2 starting point where MPBs already observed:

- **$BiFeO_3$ (rhombo.)** + **GaFeO3 (tetra.)**

(1-x)$BiFeO_3$+ x$PbTiO_3$

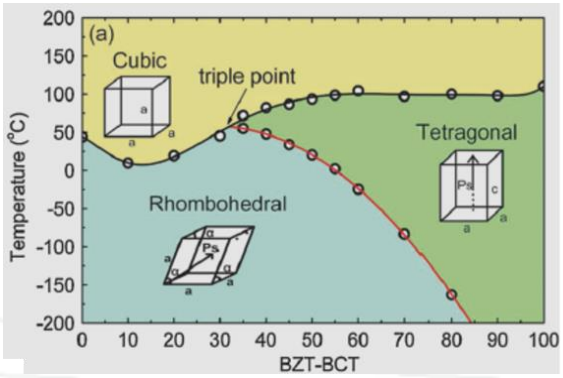


Yang et al, Materials Research Bulletin 47 (2012) 4233–4239

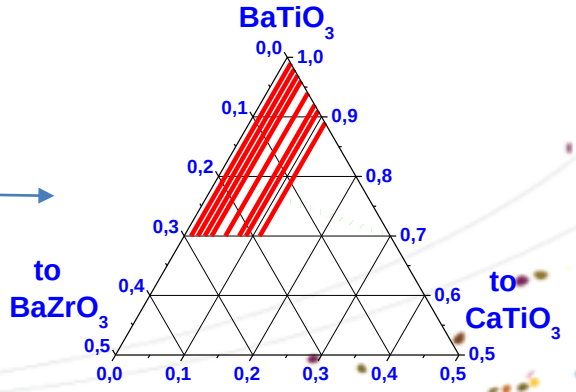


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W. Liu et al, PRL 103 (2009) 257602

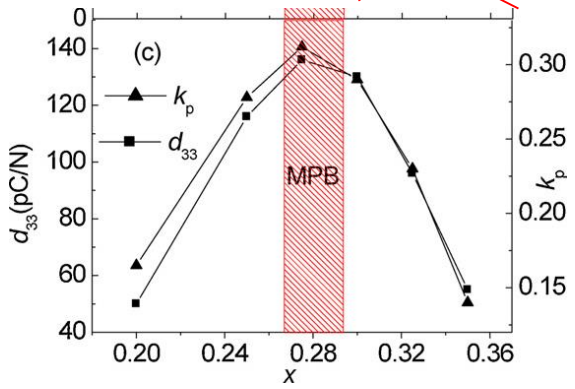


Our goal : Looking for other MPBs in lead-free solid solutions

2 starting point where MPBs already observed:

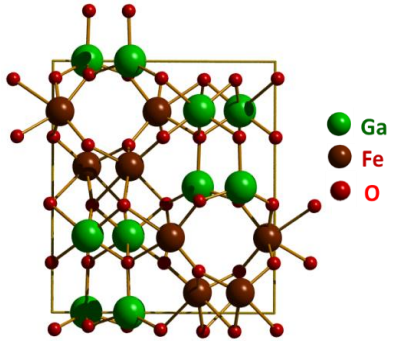
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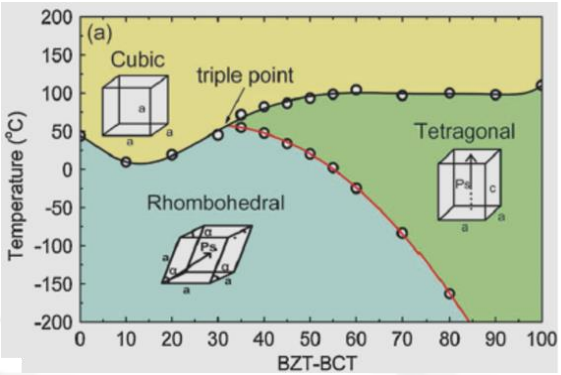
Yang et al, Materials Research Bulletin 47 (2012) 4233–4239

APR OXYMORE



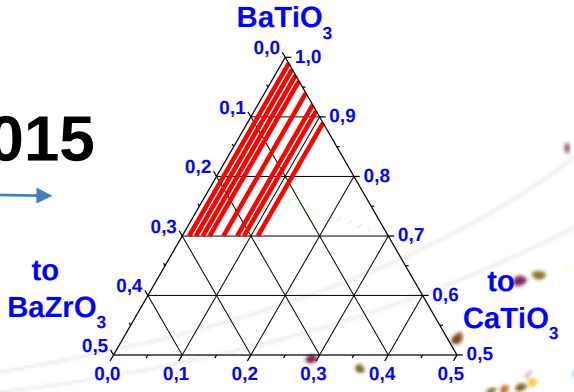
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W. Liu et al, PRL 103 (2009) 257602

FUI TOURS2015



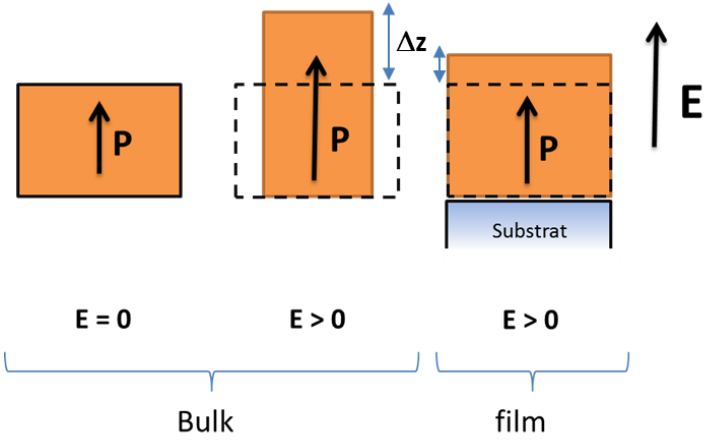
Measuring Piezo-response in thin films

D_{33} evaluation in thin films complicated by 2 limiting factors :

- Small applicable voltage
  10V / 100nm = 1MV/cm

$\Delta z = D_{33} * V$ => 1-100 pm!

- Substrate clamping



Rigid substrate model

K. Lefki and G. J. M. Dormans

Journal of Applied Physics **76**, 1764 (1994)

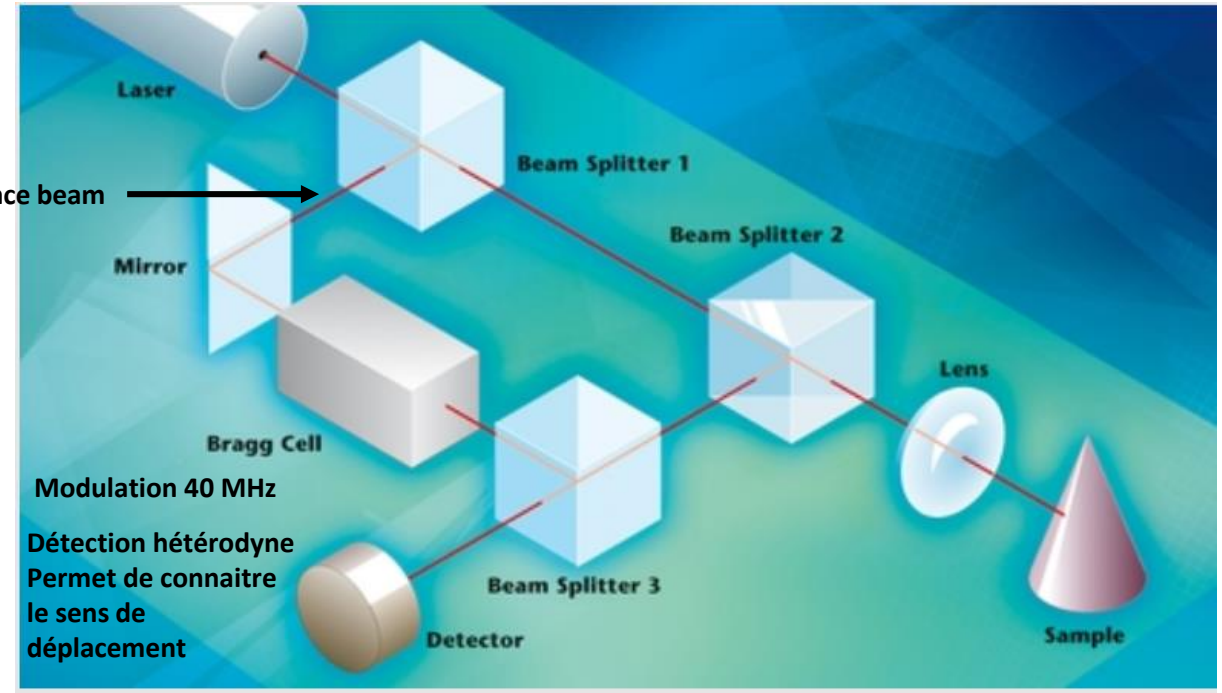
$$d_{33}^{eff} = d_{33} - \underbrace{\frac{2s_{13}^E}{s_{11}^E + s_{12}^E} d_{31}}_{>0}$$

substrate contribution

=> Small displacements to measure

Measuring Piezo-response in thin films

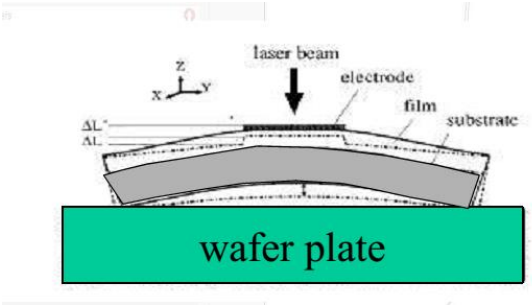
Dual Beam Laser Interferometry (Doppler effect)

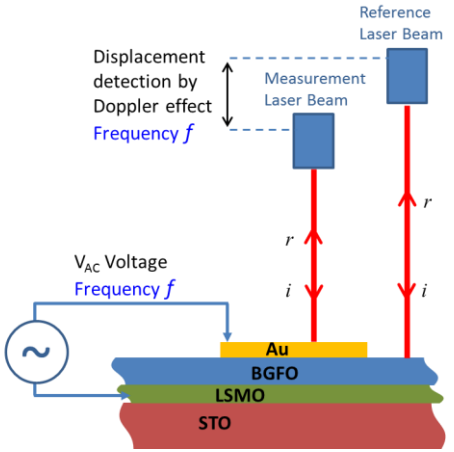


Picometric sensitivity

Measuring Piezo-response in thin films

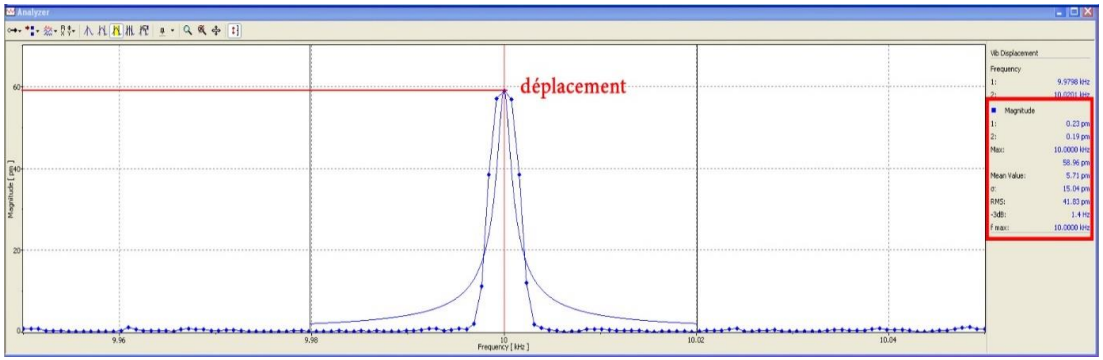
The substrate is not that rigid!
The piezoelectric film can bend it…
Substrate deformation depends on top electrode size…





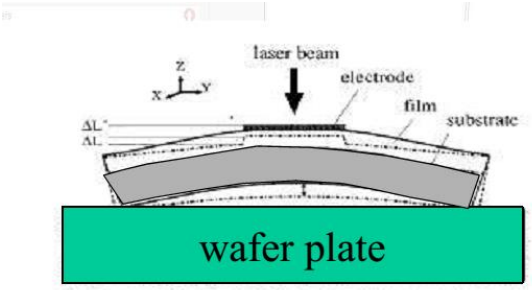
Possible solution (bandage) :

Place the reference beam beside the top electrode
⇒ Polytech MSA500



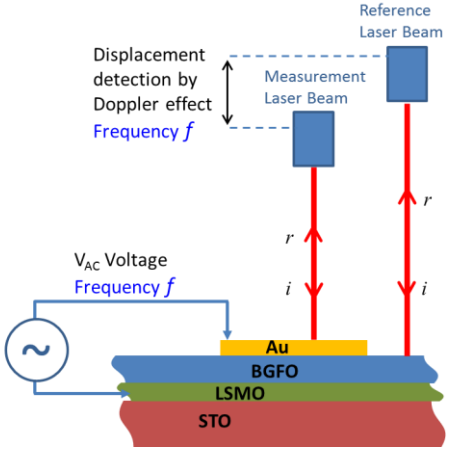
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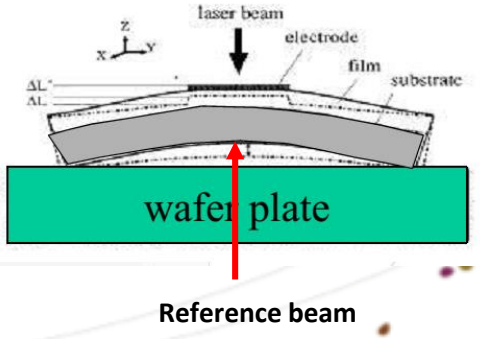
Place the reference beam beside the top electrode
⇒ Polytech MSA500



Better solution :

Place the reference beam **below** top electrode

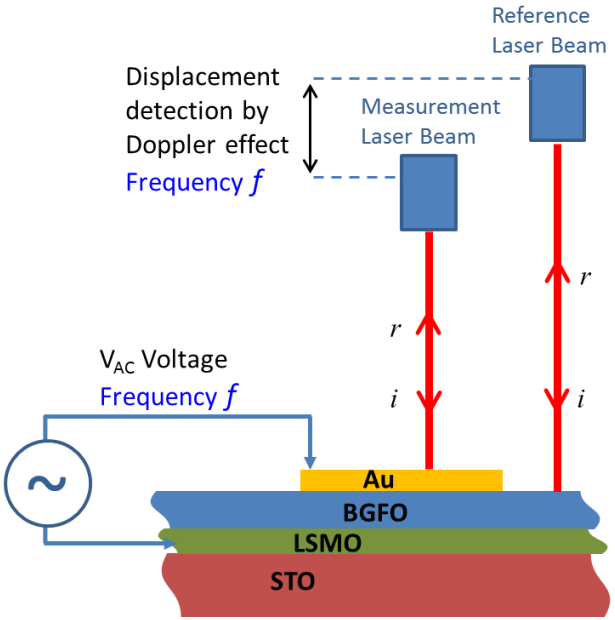
⇒ Future equipment



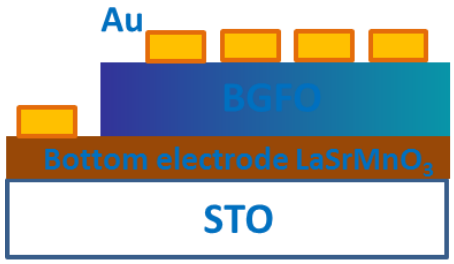
Macroscopic Piezo-response BGFO(x)

Dual Beam Laser Interferometry MSA500

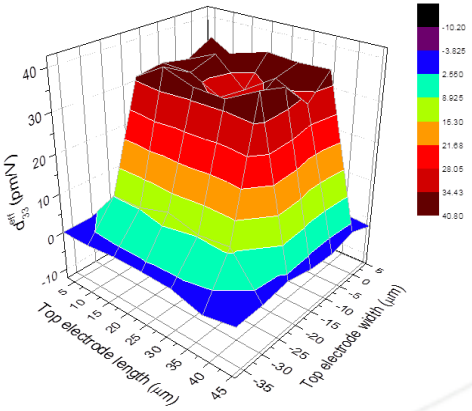
BGFO(x) 130nm/LSMO 25nm/STO

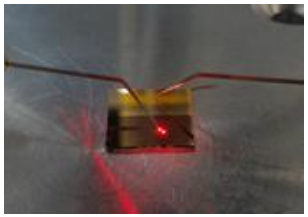


Au top electrode size =30x30 µm (200nm)



d_{33eff} mapping on and around one top electrode





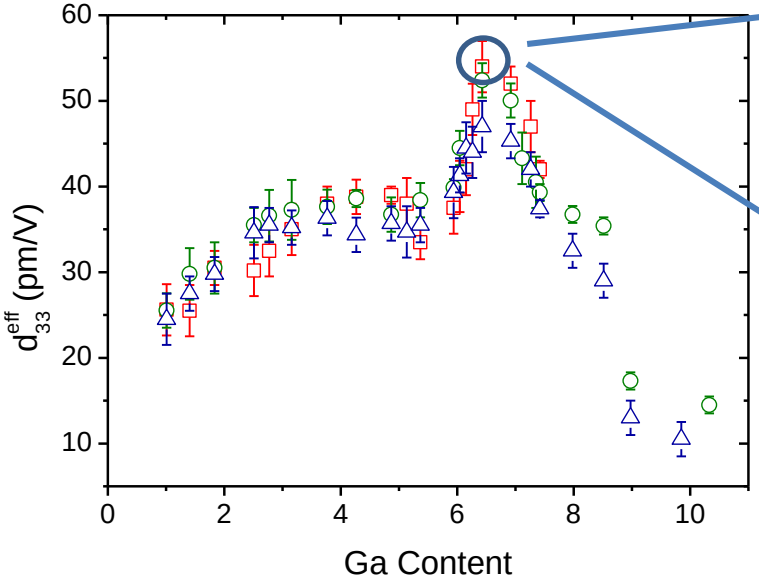
Cartographie possible avec les 2 faisceaux lasers du même côté
=> indispensable pour les CMUT

Macroscopic Piezo-response BGFO(x)

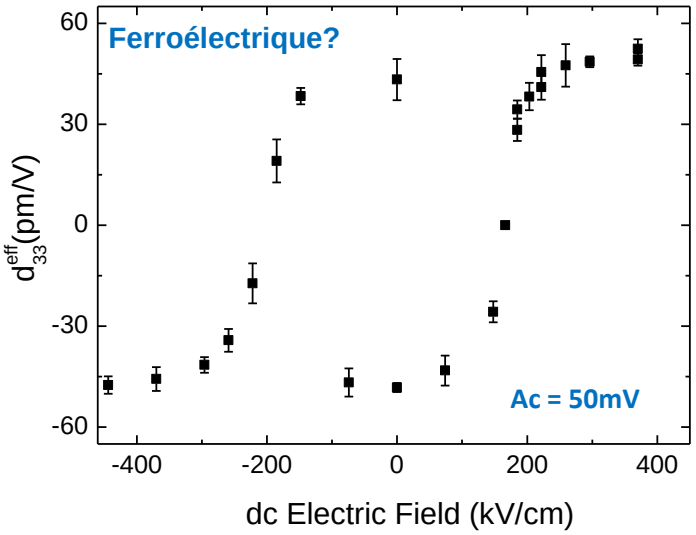
Dual Beam Laser Interferometry

BGFO(x) 130nm/LSMO 25nm/STO

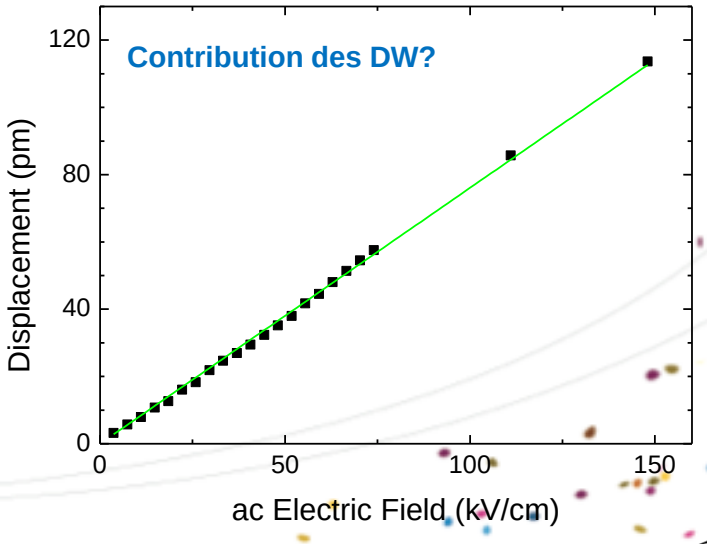
D_{33eff} Vs Ga content



D_{33}eff vs DC hysteresis loop



Displacement vs AC amplitude



Cycle d'hystérésis pas prévu sur MSA500 :

- **Réglage manuel de la tension**
- **puis programmés en VBA**
  => 15 min pour 100 points

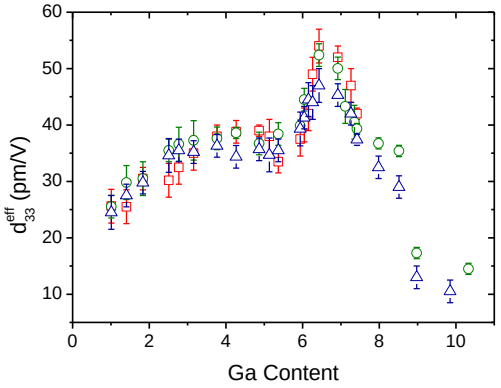
Ferroelectric loops in BGFO(x)

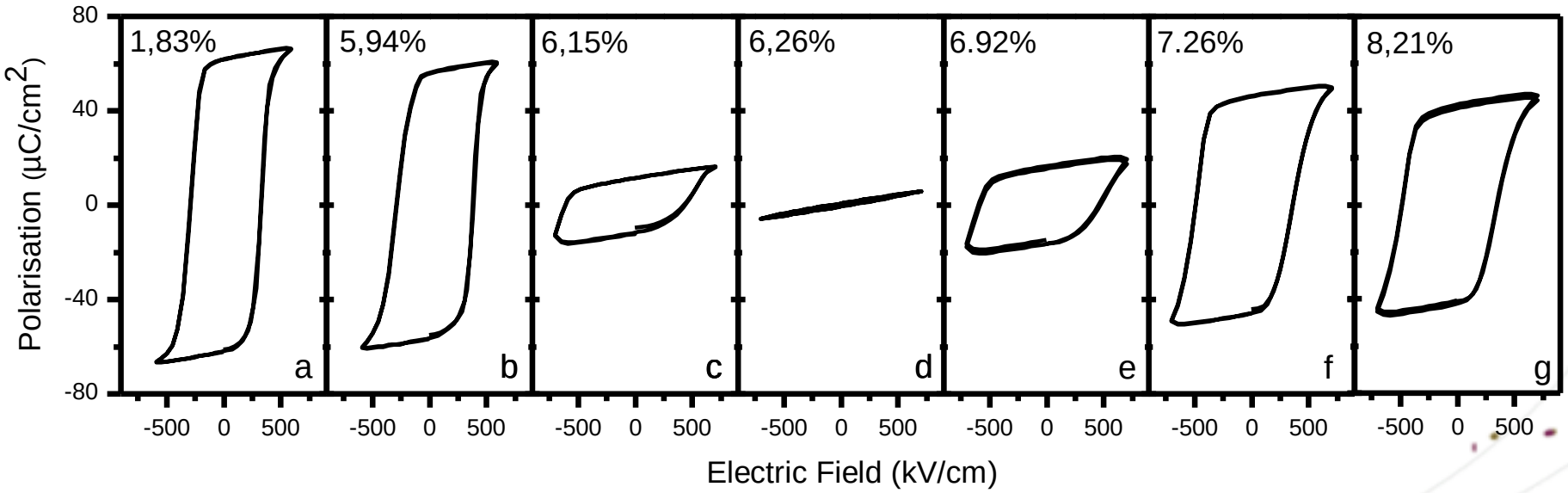
P(E) loops @ 77K

BGFO(x) 130nm/LSMO 25nm/STO

Testeur ferroélectrique RADIANT LC (Grandmont)







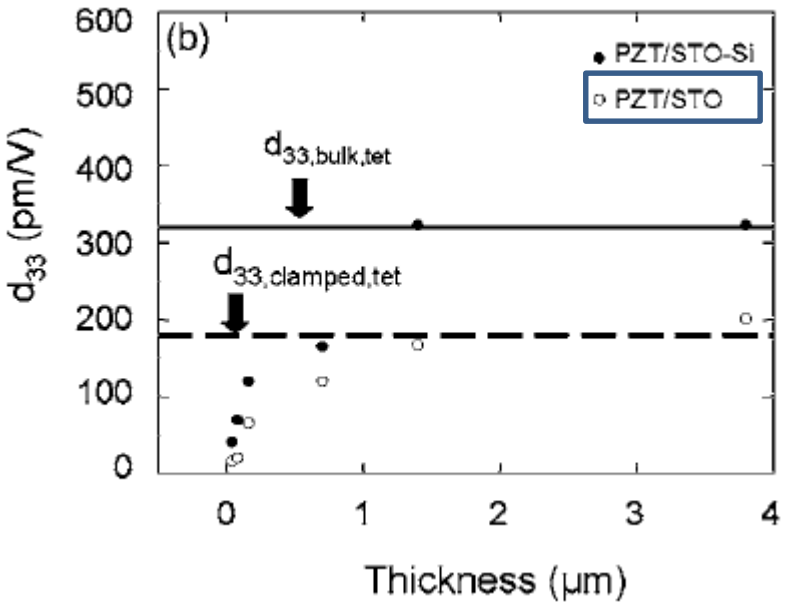
Clear transition between 2 ferroelectric states around 6.3%

Almost no P_R @ x=6.3%

Piezo-response in BGFO(6.4%) vs epitaxial PZT

Relaxation of the film reduces clamping effects

Kim et al, Appl. Phys. Lett. **88**, 142904 2006

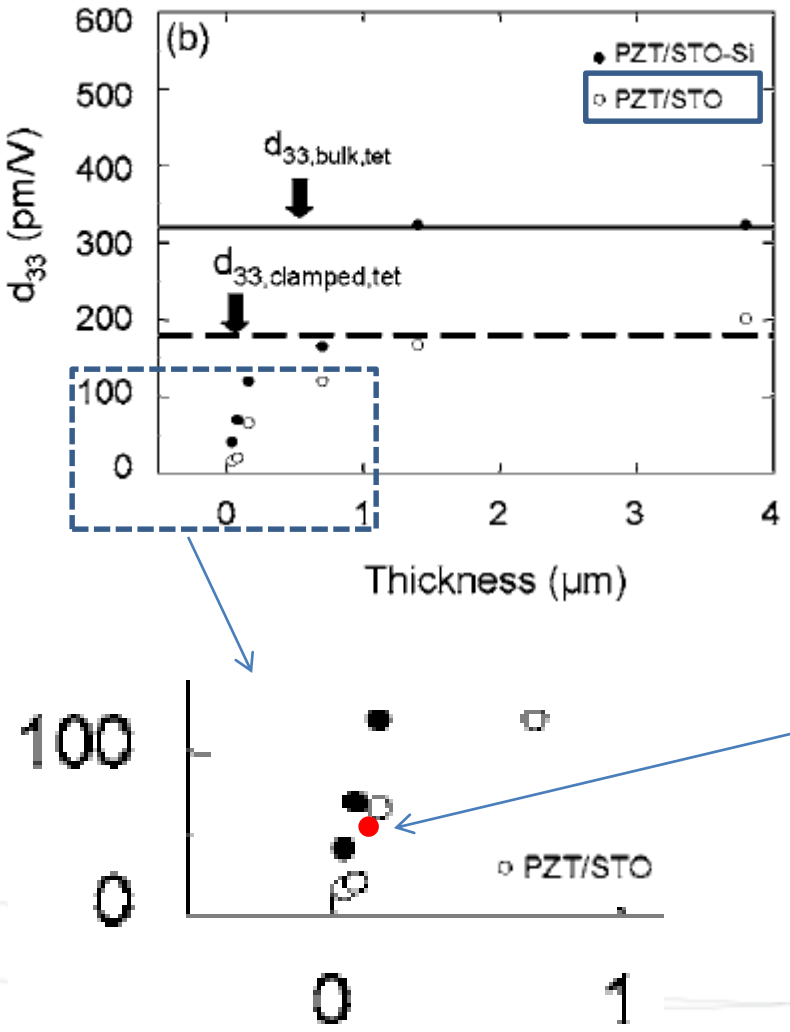


Strong influence of the film thickness on measured d_{33}

Piezo-response in BGFO(6.4%) vs epitaxial PZT

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Kim et al, Appl. Phys. Lett. **88**, 142904 2006

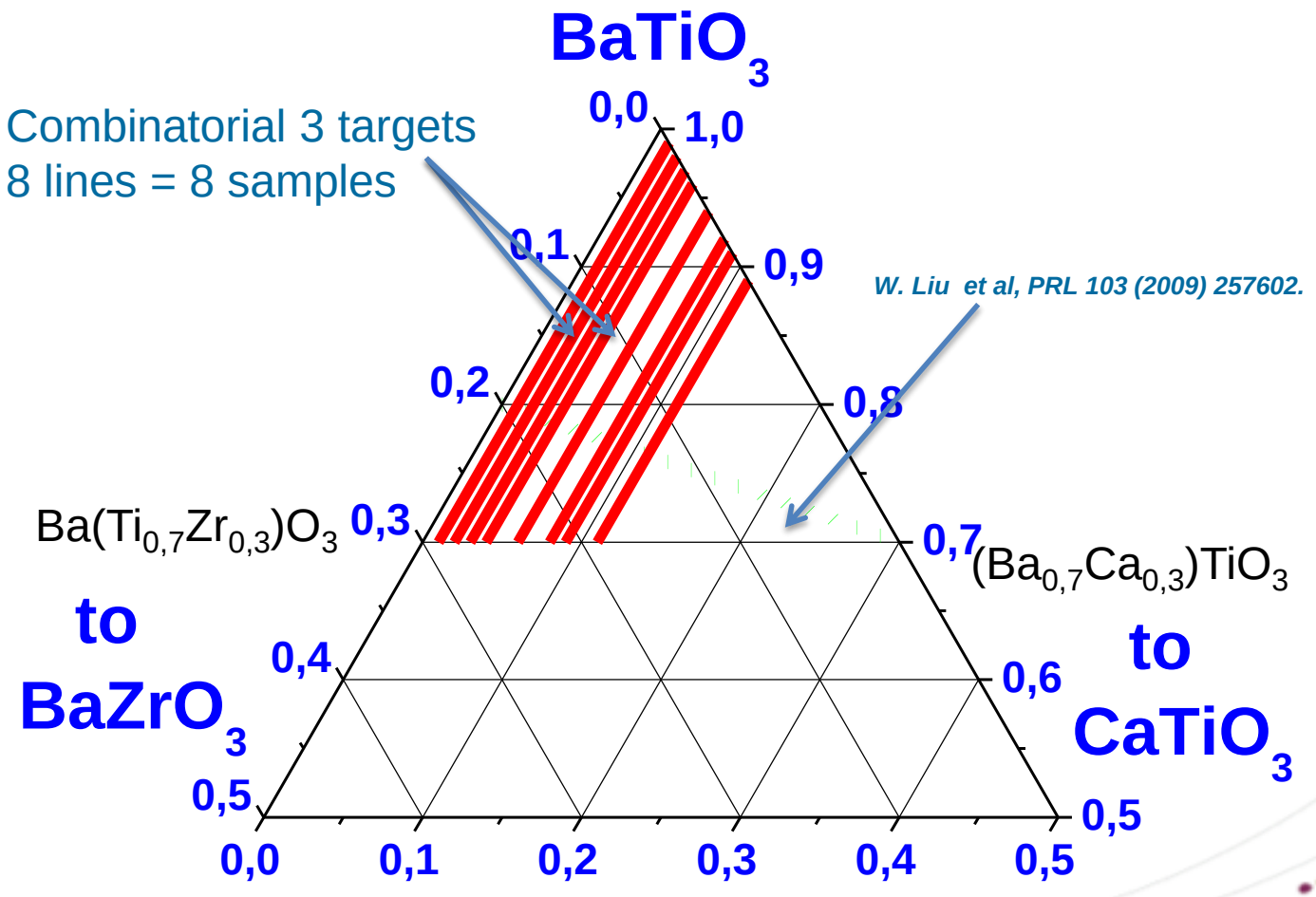


Strong influence of the film thickness on measured d_{33}

This study 55 pm/V @ 135nm
⇒ Compares with best published epitaxial PZT value

BCTZ polycristallin sur IrO_2

Screening of the ternary phase diagram:

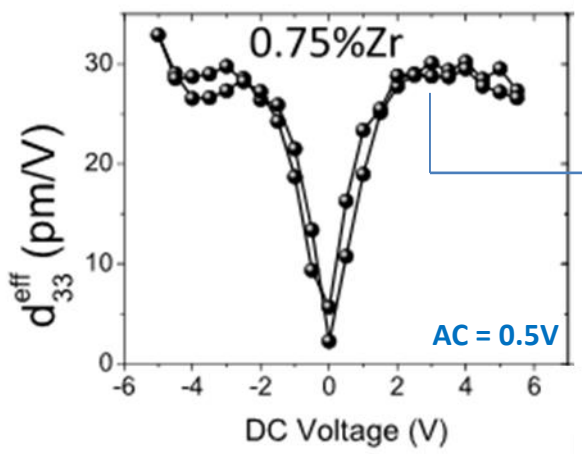


Objectives: Search for others MPB

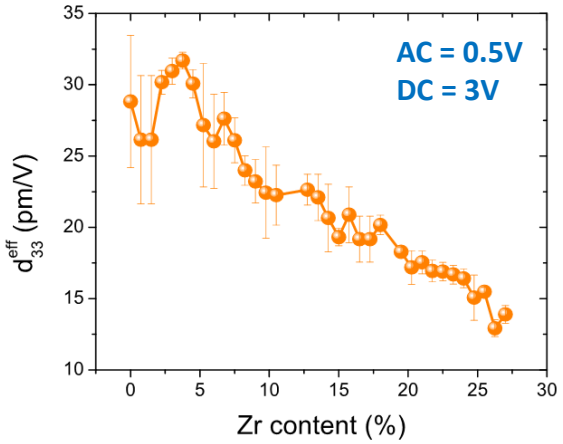
Piezoelectric properties : Ca = 3% line

Dual Beam Laser Interferometry

D_{33eff} Vs DC excitation



D_{33eff} Vs Zr content



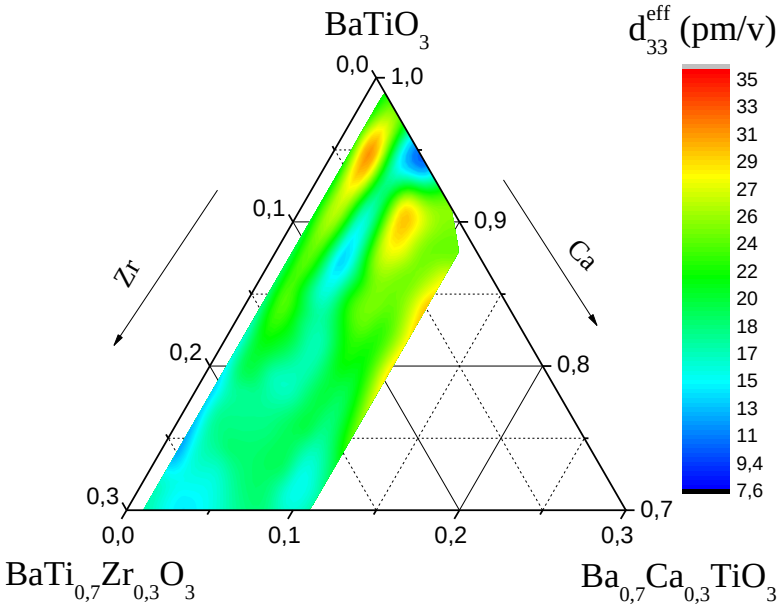
Ferroelectric @ RT but Pr~0 (polycristal.)

75 capas mesurées / ligne

Cycles automatisés VBA = 10mn (60pts)

Piezoelectric properties across all libraries

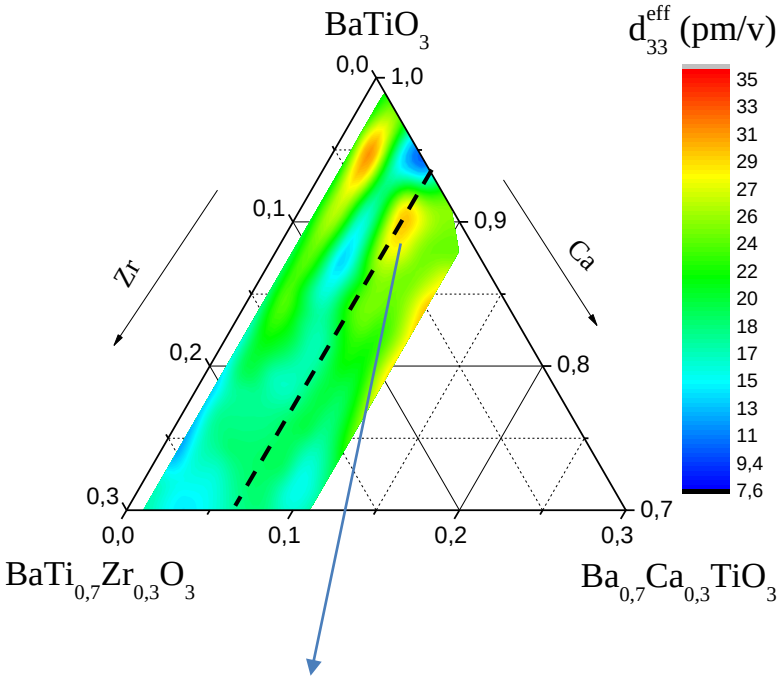
D_{33eff} map

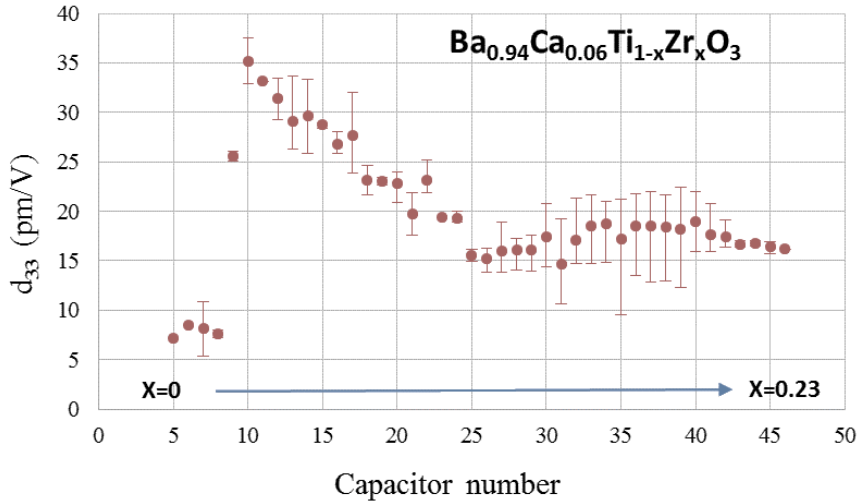


=> D_{33eff} increase probably due to the presence of a MPB

Piezoelectric properties across all libraries

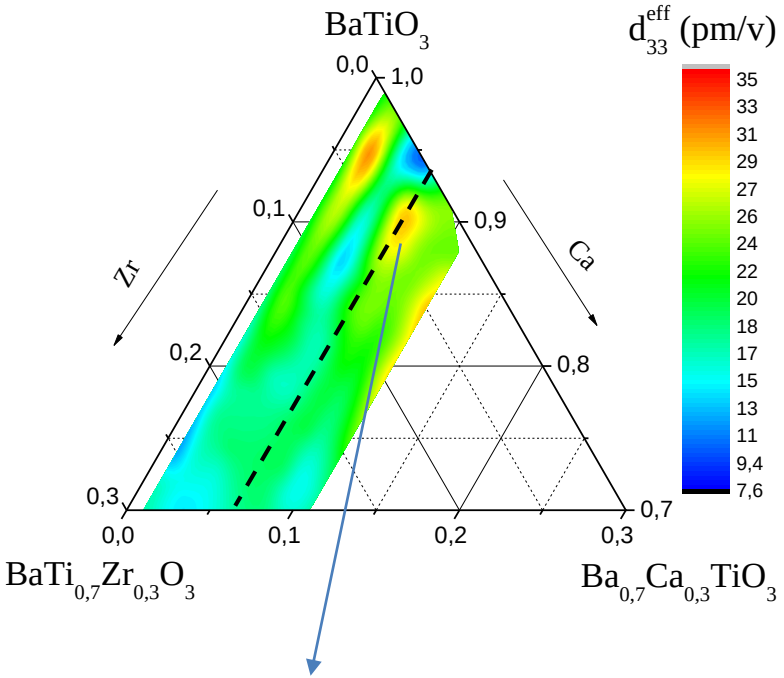
D_{33eff} map





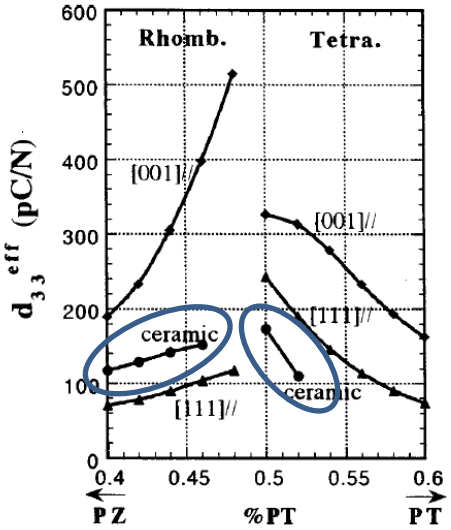
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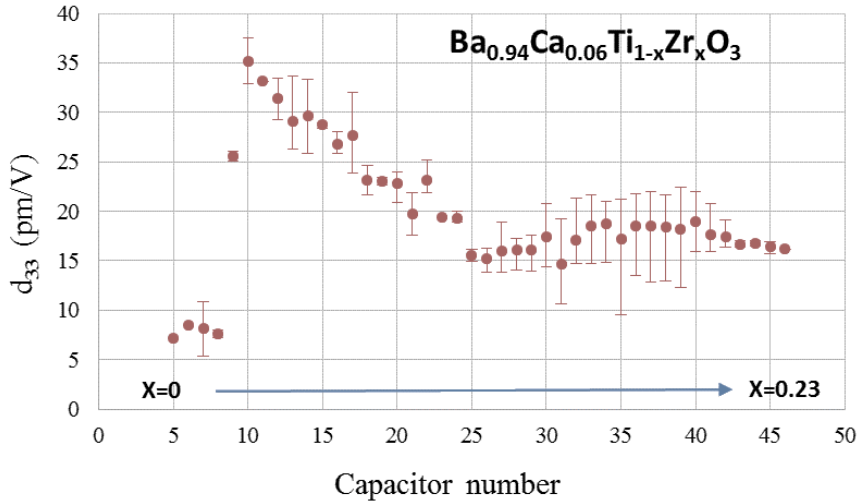
D_{33eff} map



BCTZ polycristallin => céramique

PZT





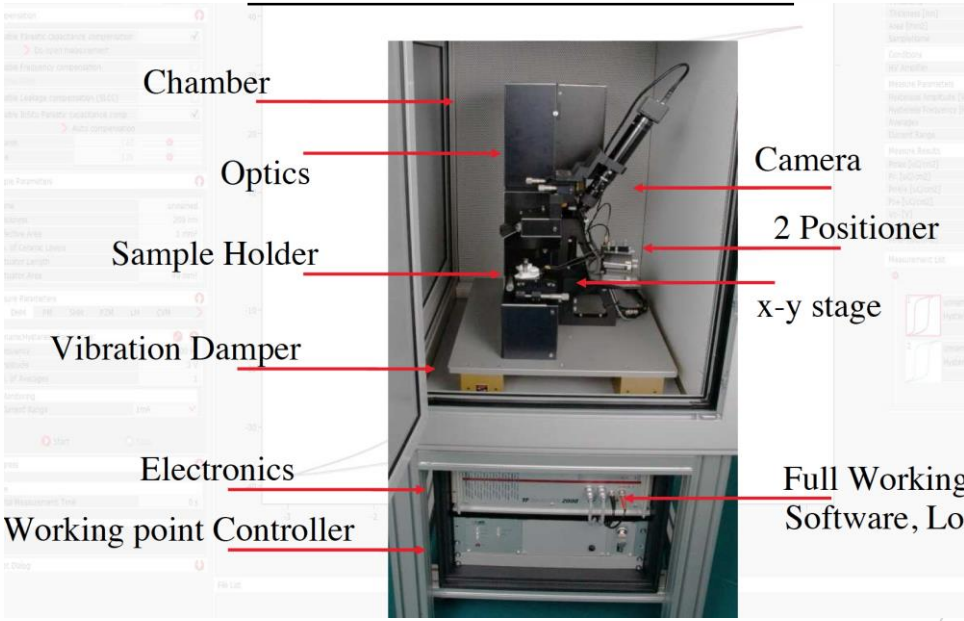
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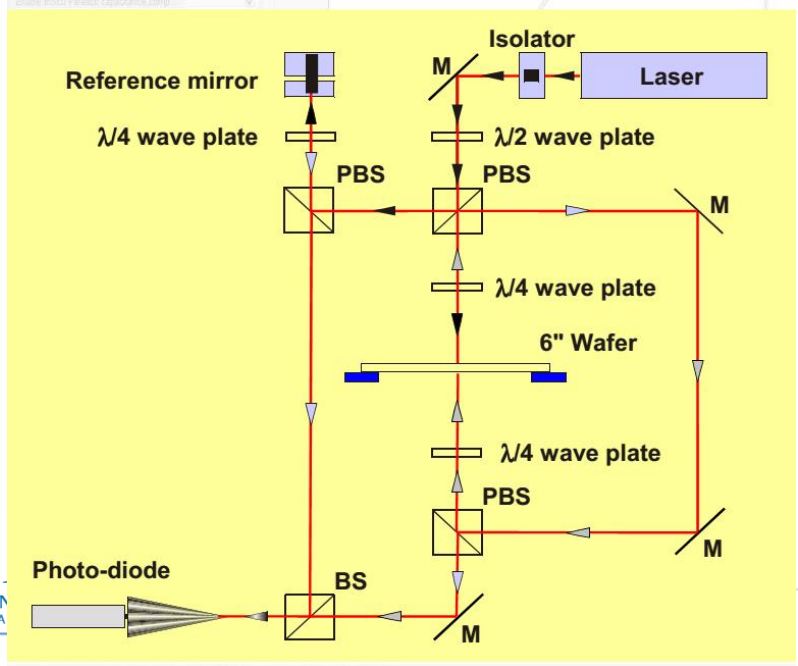
Futur banc de caractérisation

Interféromètre Laser + Mesures électriques



Version aixDBLI manuel





+ ou - 400 V (70mA)

1 mHz to 5 kHz.

- Hysteresis measurement
- PUND measurement
- Fatigue measurement
- Retention measurement
- Static hysteresis measurement
- Imprint measurement
- Leakage current measurement

and optional

- C(V) measurement

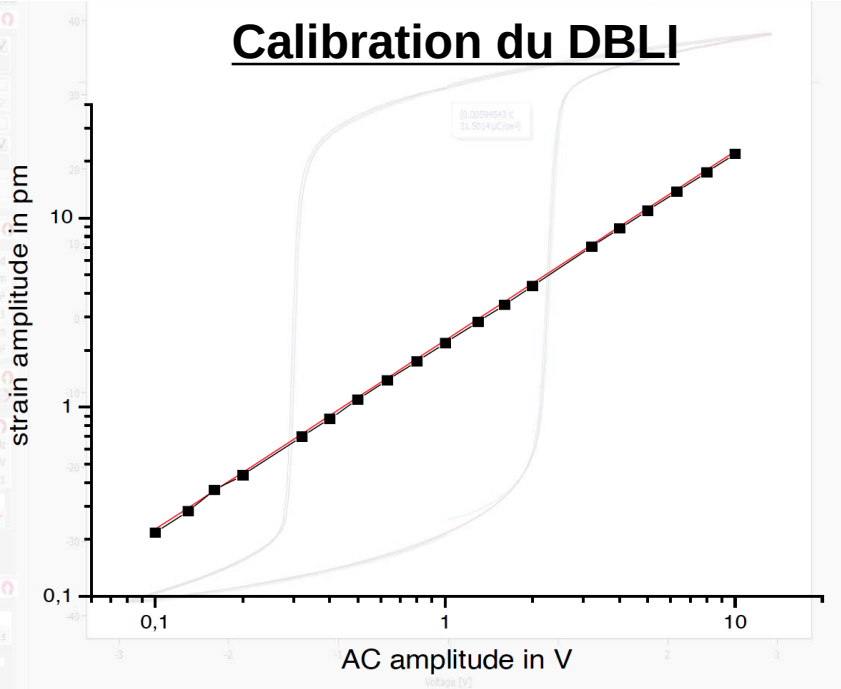
Banc de caractérisation

Films fins et mesures de $d_{33,f}$

Quelques caractéristiques

- résolution de 1 pm minimum
- mesures rapides (quelques secondes);
- Mesures possibles sur des plaquettes 6 pouces.

Calibration du DBLI



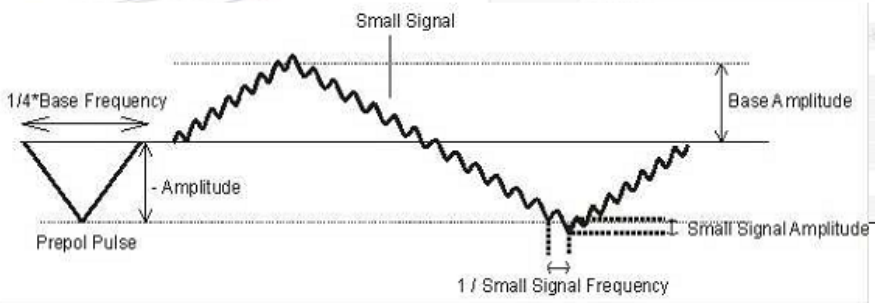
Echantillon de quartz

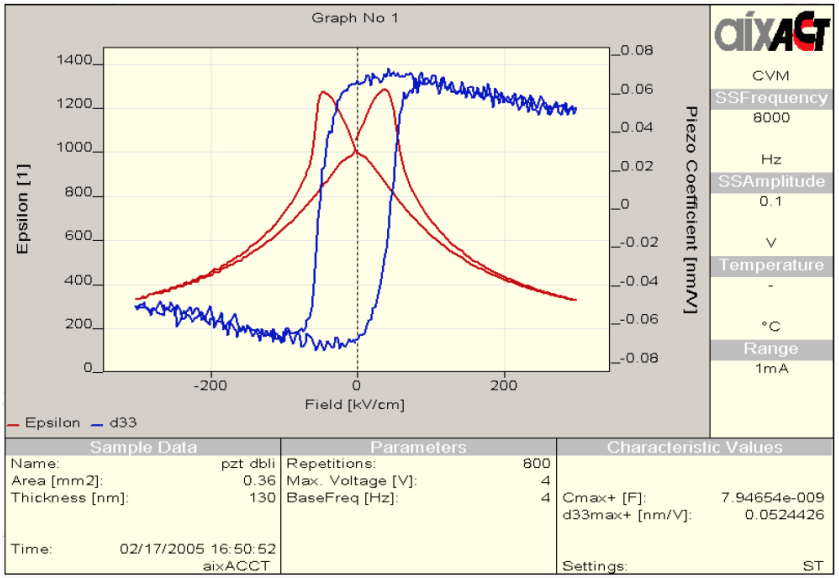
Banc de caractérisation

Films fins : mesures de $d_{33,f}$ et permittivité

Mesures petits signaux

dielectric (ε_{33}) and effective piezoelectric ($d_{33,f}$) coefficient





On mesure la réponse à la fréquence d'excitation (small signal) => lock-in

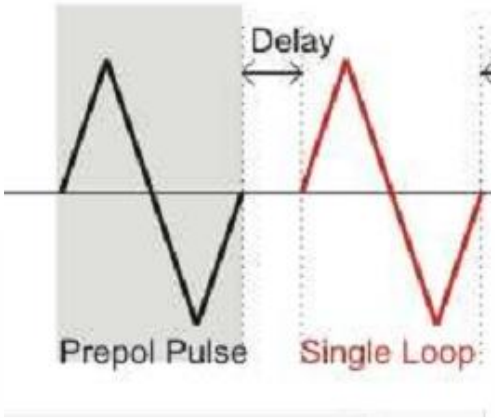
- Mesure de la variation de charge => C puis ε
- Mesure du déplacement => $d_{33,f}$

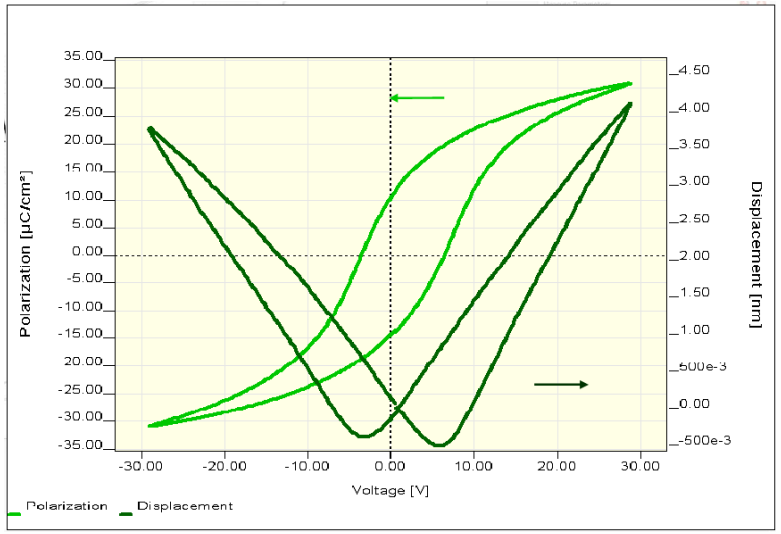
Les 2 cycles en quelques secondes…

Banc de caractérisation

Films fins : mesures de polarisation et allongement

Mesures grand signaux





On mesure la réponse à la fréquence d'excitation fort signal

- Mesure de la variation de charge => polarisation
- Mesure du déplacement => allongement

Les 2 cycles en quelques secondes…

CONCLUSION

- Plateforme complète contenant deux systèmes séparés mais basés sur une même configuration pour l'outil de pilotage;

- Utilisable pour différentes formes et épaisseurs de matériaux piézoélectriques;

- Optimisation des paramètres pour diverses applications.