Structuration of zero-shrinkage LTCC using mineral sacrificial materials

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Outline

ÉCOLE POLYTECHNIQUE
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1. Introduction - Thick-film / LTCC structuration techniques
2. Mineral sacrificial pastes - Requirements & formulation
3. New sacrificial materials - Thick-film structures
4. LTCC structures - Processing and results
5. Conclusions & outlook

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1. Applications : cantilever & bridge

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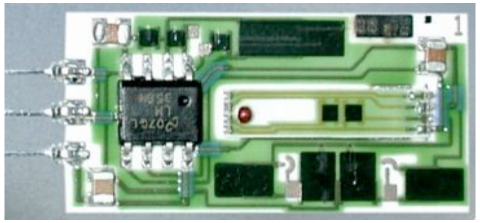
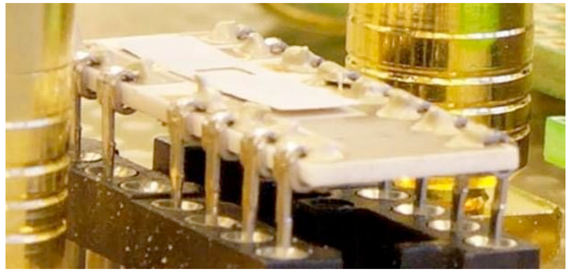
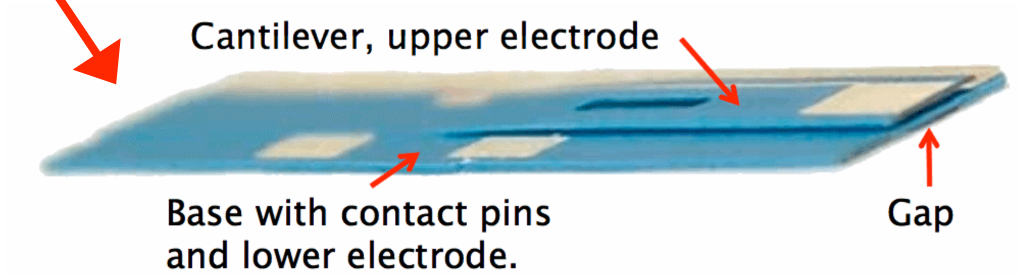
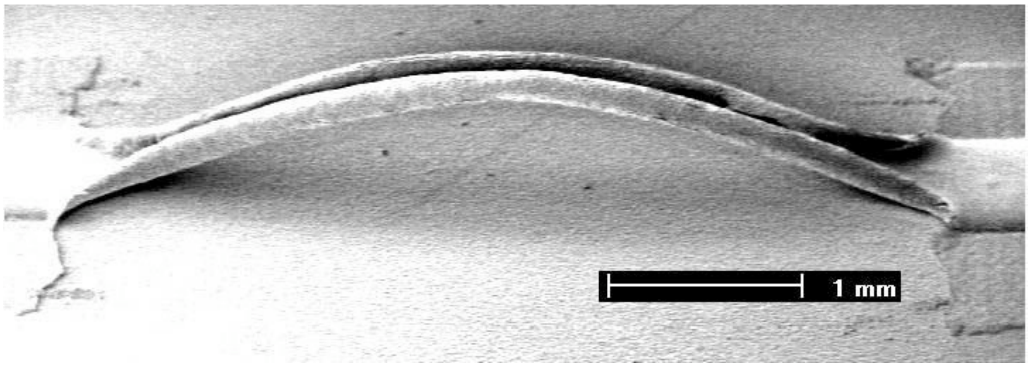
- Micro-force sensors
  - Thick-film or LTCC
  - Mineral sacrificial paste etched by acid





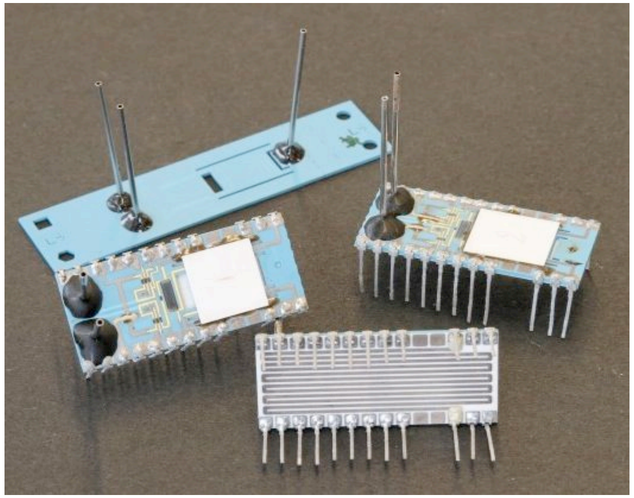


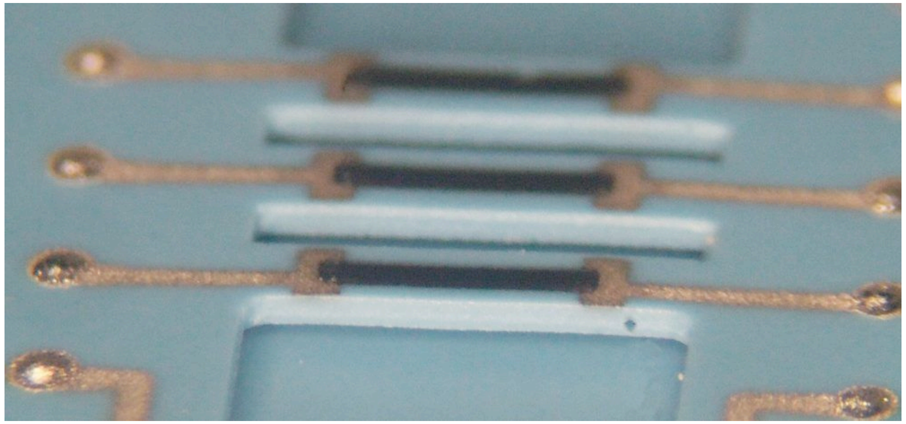
- Suspended thermistor
  - Flow sensing
  - Thermal actuator
  - Igniter
    - μ-Thruster
    - SOFC

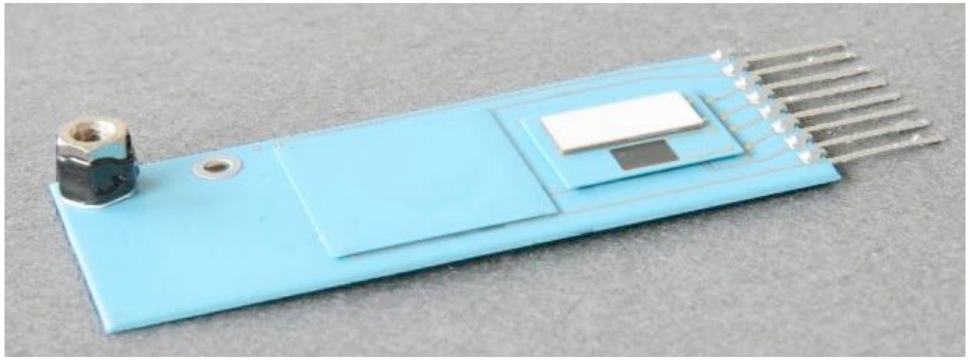


1. Applications : fluidics

- Chemical reactor
- Flowmeter
- Gas viscosity sensor







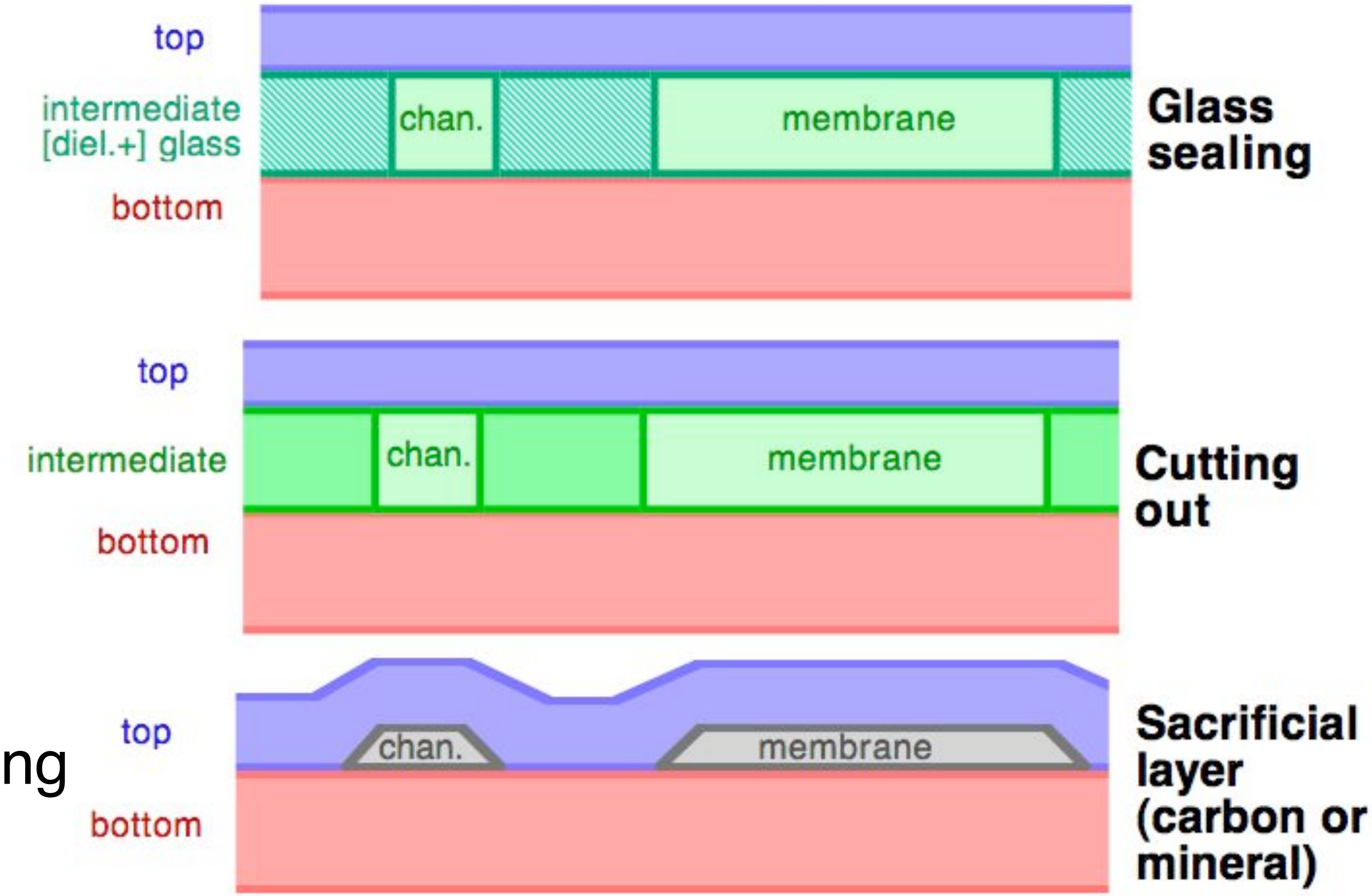
1. Structuration methods

Features

- Vias
- Channels
- Membranes
- Beams

Three types

1) Glass sealing
2) Cutting & stacking
3) Sacrificial layer



1. LTCC vs. alumina for sensors

Material	LTCC (DP 951)	Al_2O_3 (96%)	Ratio
Minimal thickness [mm]	0.04	0.17	*0.24*
Short-term strength [MPa]	320	600	*0.53*
10 year strength [MPa]	110	270	*0.41*
Young's modulus [GPa]	110	320	*0.34*
Thermal conductivity [W/m]	3	25	*0.12*
Design strain [ppm]	1'000	800	*1.25*
Flexural sensitivity [kN^{-1}]	5.68	0.11	*53*
Thermal resistance [K/W]	8'333	235	*35*

- LTCC for thermal & low-range mechanical sensors
- **Thick-film dielectric ≈ LTCC**

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2. Mineral sacrificial paste vs. carbon

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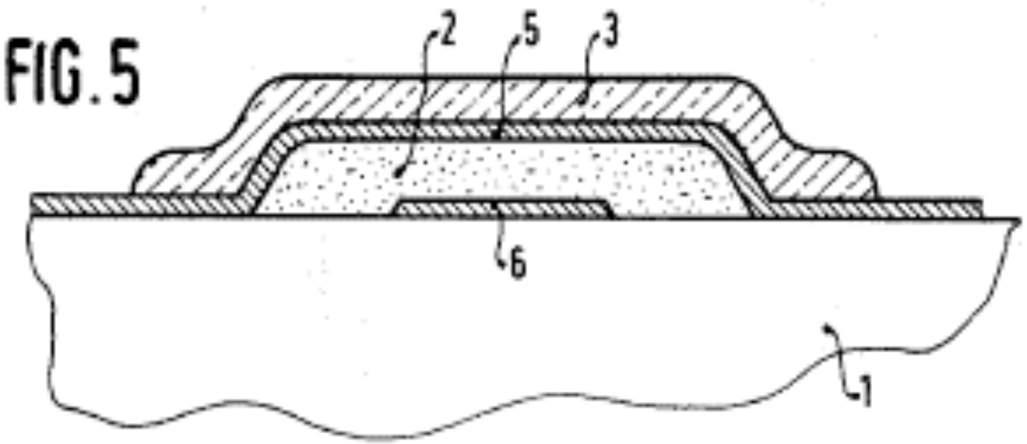
- Pioneering work in in the 1980's: **std. thick-film tech.**
  - Stecher et al., Bosch, Germany
  - Thick-film dielectric on carbon sacrificial paste
  - Alumina substrate
  - Complex steps to avoid sagging / swelling (N_2, then air)
  - Already thought about using mineral sacrificial paste (MSP)!
- Too complex
- ➢ Did not catch on

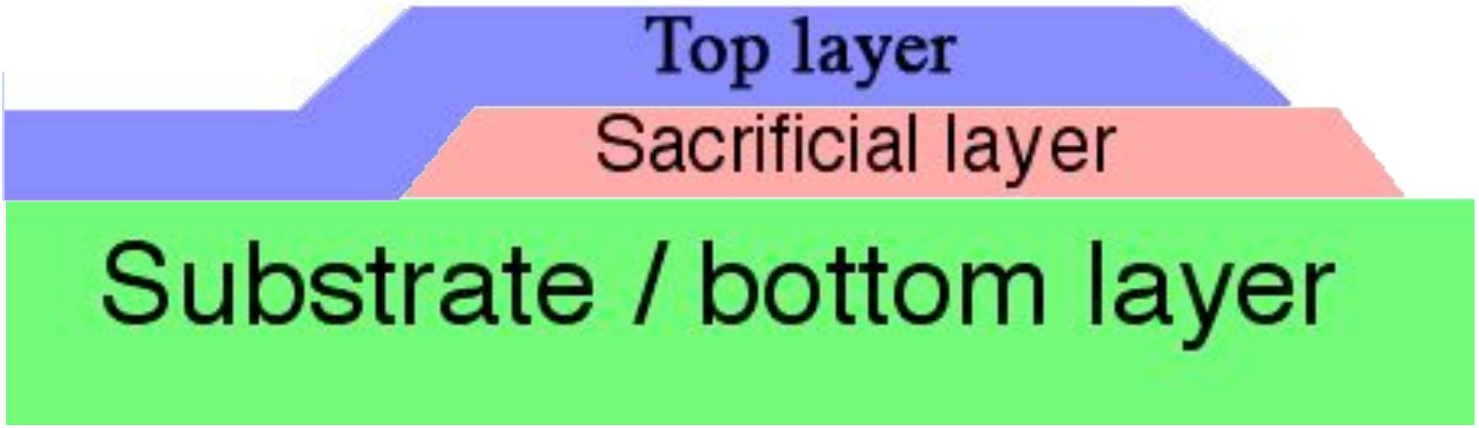
FIG. 5



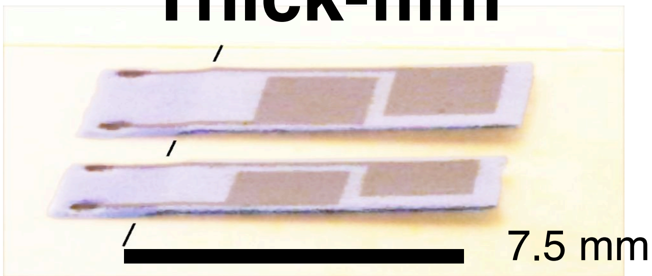
2. Mineral sacrificial paste - process

- Print [fire] mineral sacrificial paste (MSP) onto LTCC / ceramic substrate
- Laminate (LTCC) / print (ceramic) top layer
- Fire structure (co- or post-fire)
- Chemically etch sacrificial layer - typ. **acetic / phosphoric acid**

→ Requires relatively "open" structure



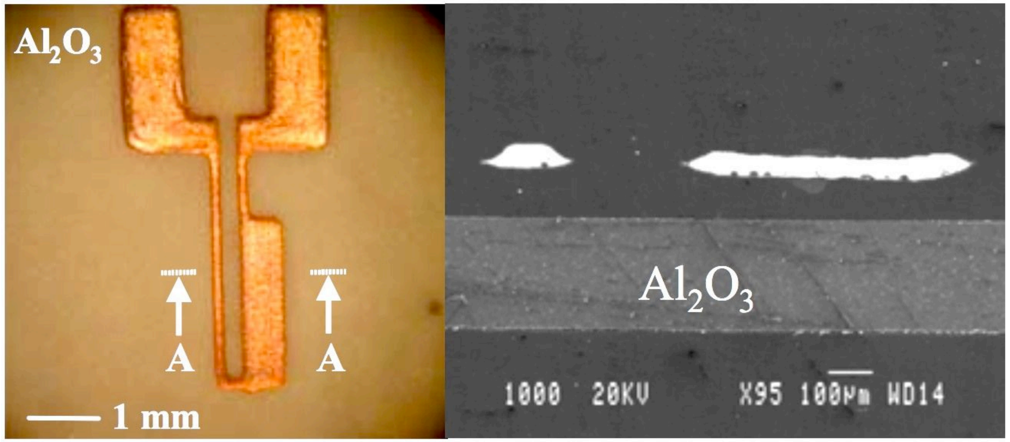
2. MSP requirements - thick-film & LTCC

Property	Thick-film	LTCC
		
Cohesion in fired state	Required (post) Desirable (co)	Desirable (avoid peeling)
Paste formulation	Allow overprinting	Not critical (except thin LTCC)
Shrinkage matching	Not critical	Required

2. Recent work : $SrCO_3$

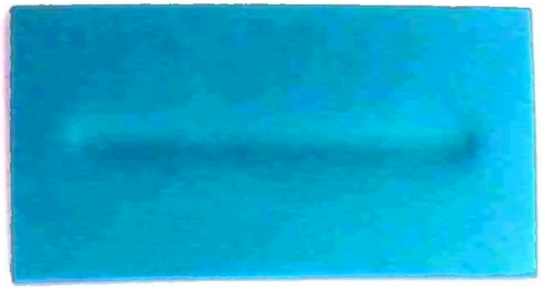
- **Thick-film** : Lucat, Ginet & al. (2006-2007)
  - $SrCO_3$ doesn't dissociate at <1000°C, quite inert
  - CO_2 evolved in acid etching
  - No shrinkage: not compatible with std. LTCC
  - No cohesion / sintering: only co-fire
  - Situation quite similar to LTCC

2007 Lucat (Thick-film ; co-fired)

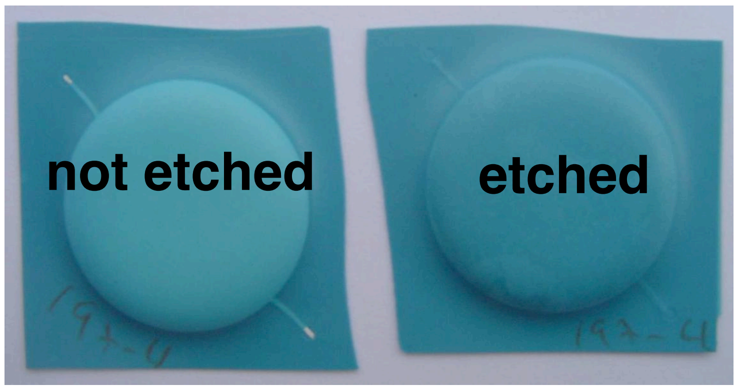


2. Recent work : $CaCO_3/CaO + B_2O_3$

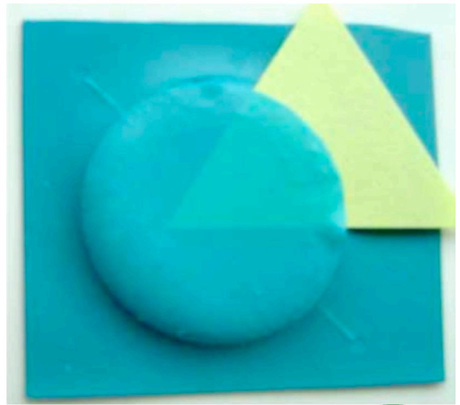
- **LTCC+thick-film**: Birol,Fournier et al. (2005-2007)
  - Firing: dissociation of $CaCO_3$ to $CaO + CO_2$
  - CaO hydrates to $Ca(OH)_2$ - **must etch fast**
  - Large amount not allowed - **reaction**
  - Good dissolution in acids ✓
  - Some limited cohesion (✓)
  - Little sintering (<10%) : **incompatible with std. LTCC**



Sintered LTCC + MSP (reverse side)

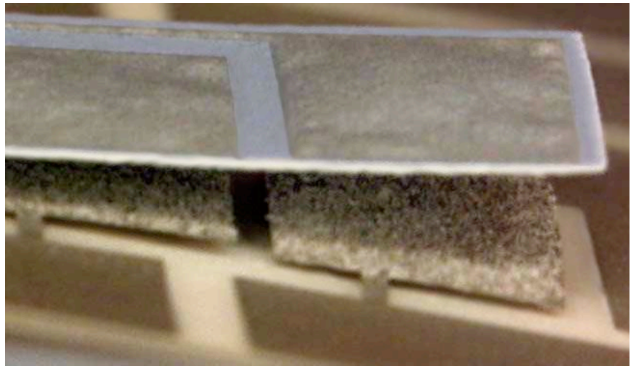


2006 Birol (LTCC)

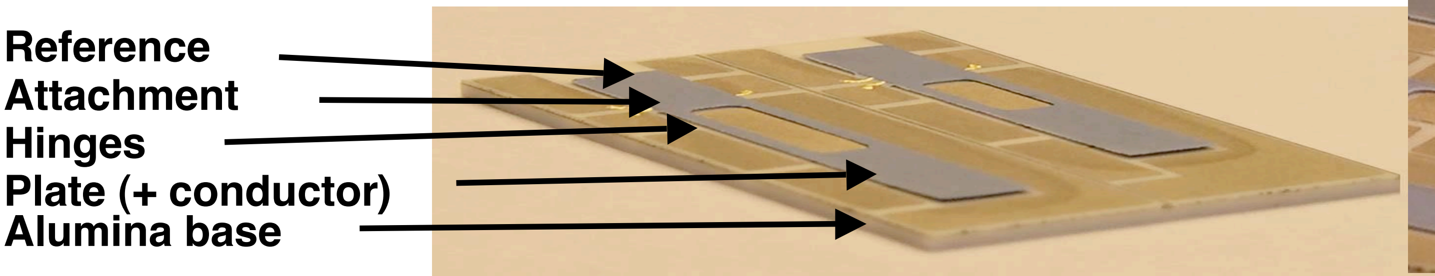


2. Recent work : CaO + borax

- **Thick-film**: Fournier et al. (2006-2007)
  - B_2O_3 replaced by borax: less volatile, melts at ≈740°C ✓
  - More dense and cohesive, can achieve good sintering ✓
  - **High contents → problems**:
    - Slower dissolution in acids
    - Excessive reactions



Thick-film dielectric (ESL 4913) *μ*-force sensor



2. Recent work : $CaCO_3$ + carbon

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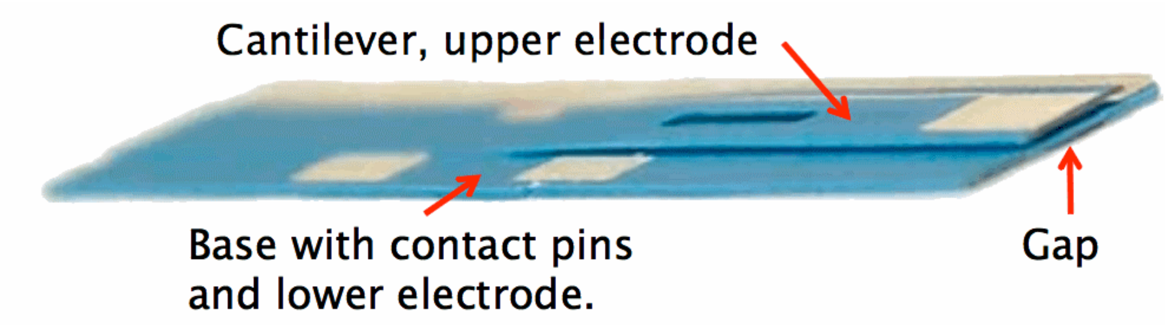
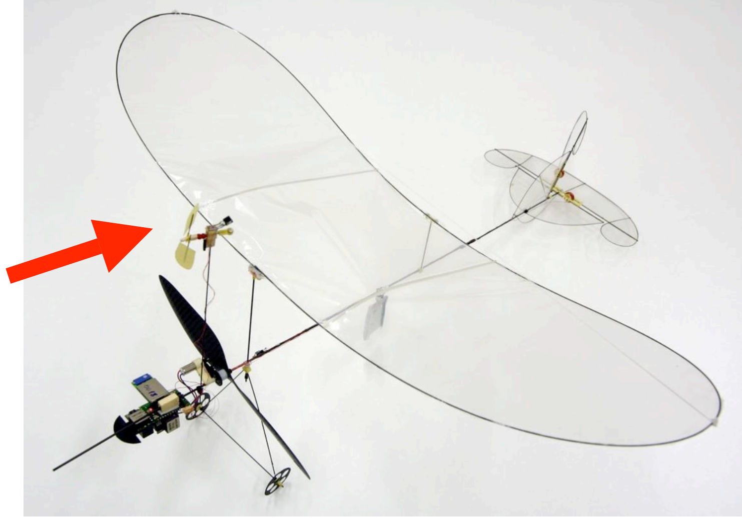
- **LTCC**: Fournier et al. (2008)
  - Decomposition of $CaCO_3$ gives some shrinkage
  - Additional shrinkage introduced with carbon
  - Can ± match LTCC shrinkage but **must add 2/3 carbon**
  - **No cohesion**



LTCC (DuPont 951) *μ*-force sensor



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3. New materials: MgO + CaB_2O_4

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- **MgO - magnesium oxide**
  - Alkaline earth oxide - similar to CaO / SrO
  - Oxide reasonably stable vs. humidity ("dead burned")
  - Well-known in MEMS literature (surface micromachining)
  - No sintering at common firing temperatures → **Zero-shrinkage LTCC**
- **CaB_2O_4**
  - Available as $CaB_2O4 \cdot 2H_2O$
  - Significant sintering & cohesion → **Standard LTCC**
  - Issues with high B_2O_3 + H_2O contents
- **Mixes: intermediate properties**

3. MgO + thick-film process

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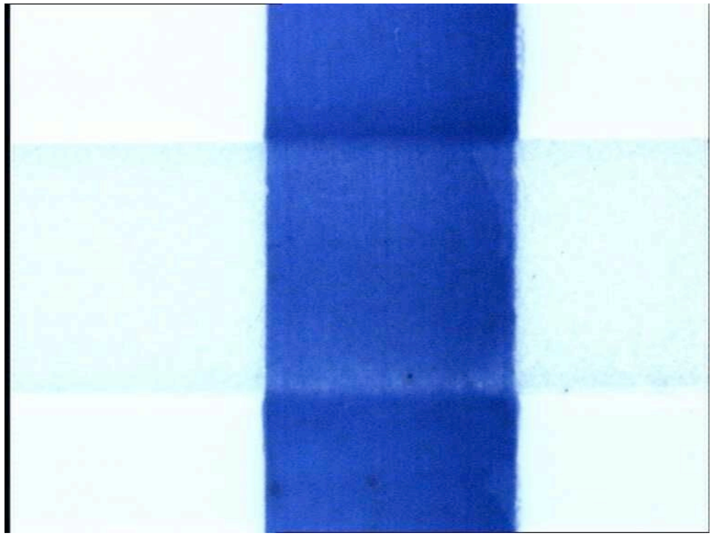
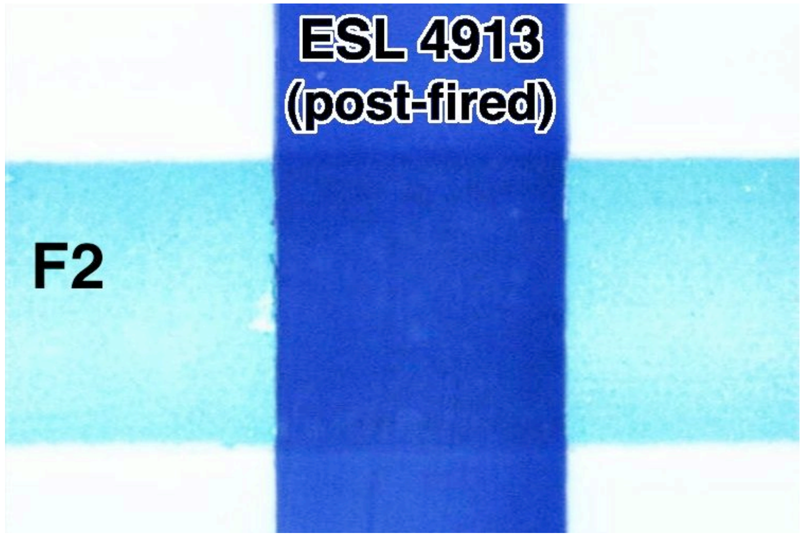
- **Sequential firing of MSP + dielectric**
  - B_2O_3 or some borax ($Na_4B_2O_7$): cohesion
  - Dielectric paste adapted to porous underlayer (LTCC: ✓)
  - No lateral shrinkage ≈ zero-shrinkage LTCC

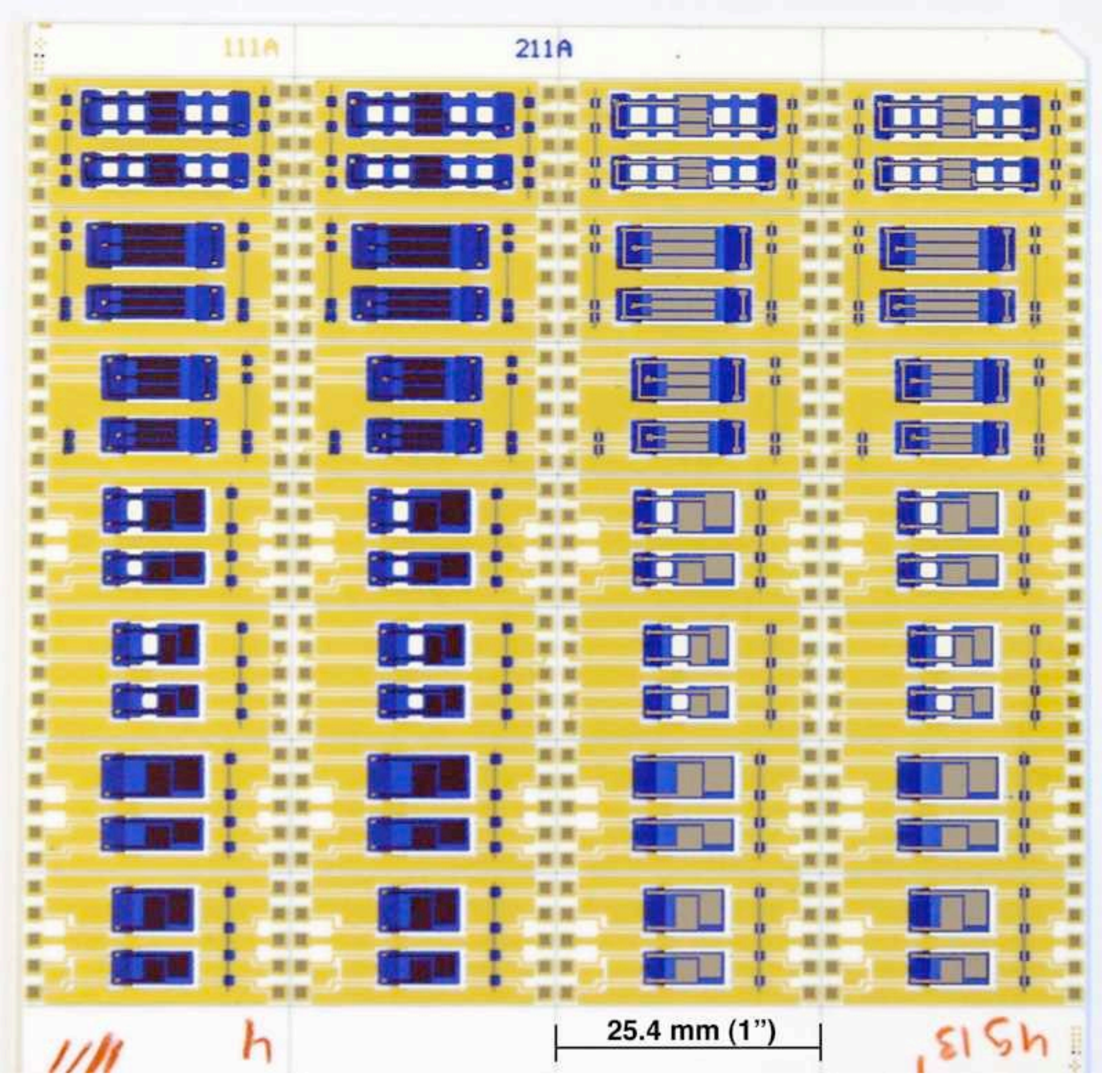


ESL 4913 over MgO + borax

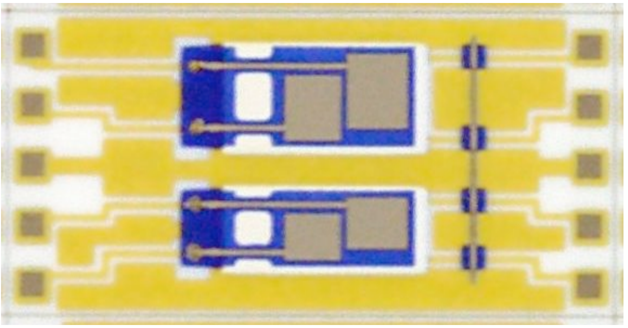


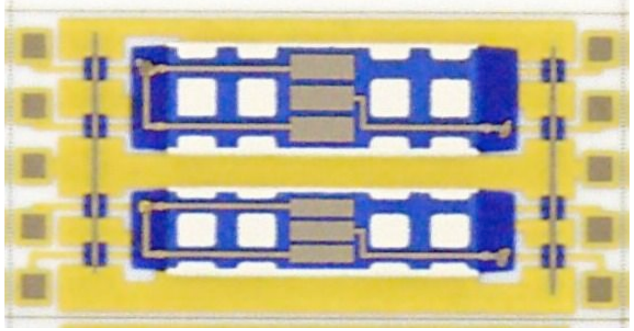
ESL 4913 over MgO + B_2O_3

3. MgO + thick-film test structures



- Structures for capacitive force sensors / actuators
- Cantilevers or bridges
- Different sizes / shapes





3. Sacrificial layer removal

- Dip into acid (≈ 1 day) @ RT
  - MgO not very reactive
  - "Dead-burned" or additives on surface
  - 10% phosphoric or acetic acid not optimised
- Rinse with tap water
- Neutralise acid with TRIS buffer
- Rinse with deionised water
- Rinse with isopropanol
- Dry @ 60°C in oven

3. MgO + thick-film process

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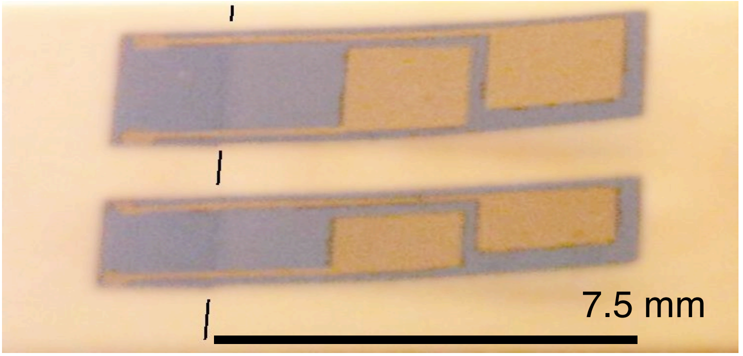
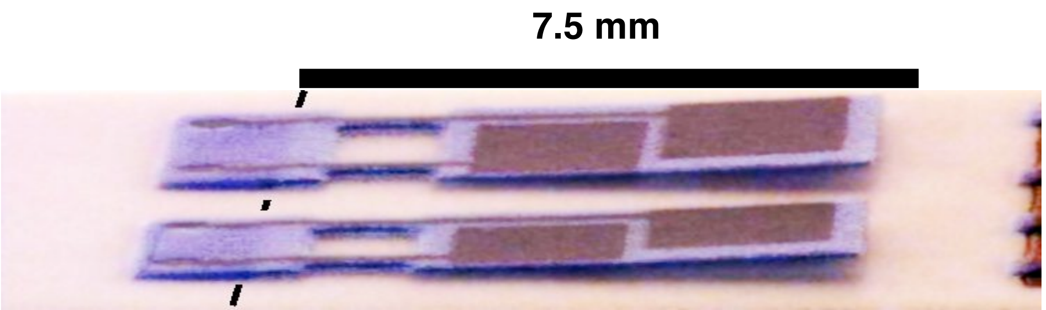
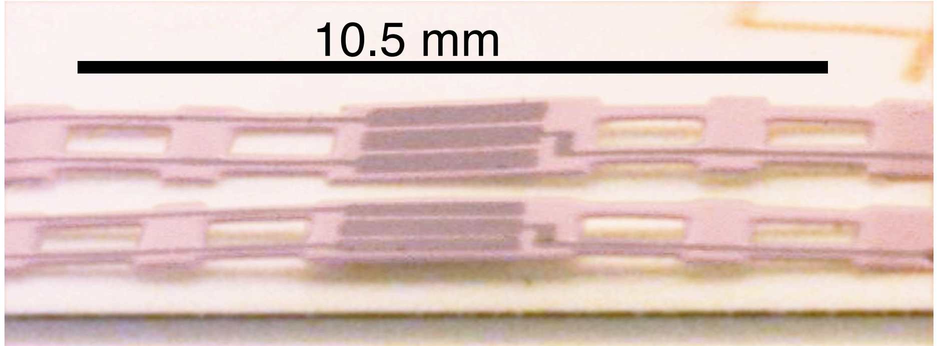
- **Achievements**
  - Very slender structures
  - Straightforward process
  - Dielectrics : good acid resistance
- **Issues**
  - Differential TCE with alumina (bridges)
  - Internal stresses: metallisation - dielectric



ESL 4913 cantilevers



ESL 4913 cantilevers



ESL 4903 bridges

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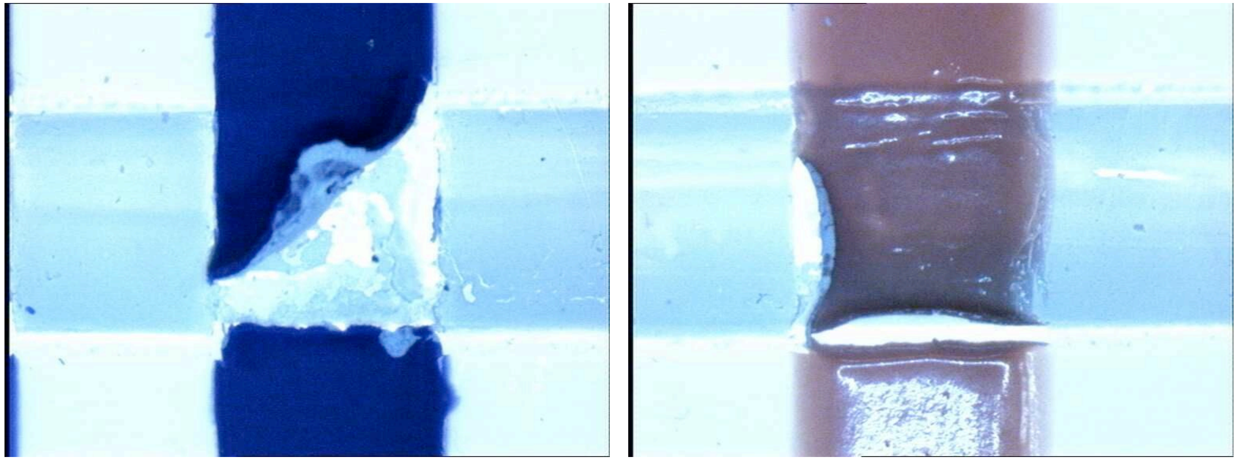
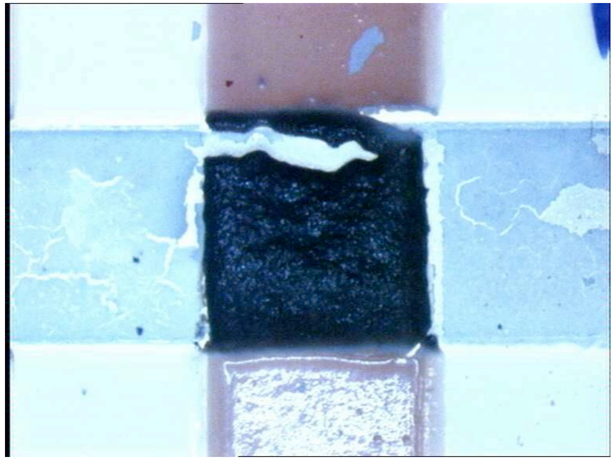
4. $MgO + H_3BO_3$ - co-firing issues



ESL 4913 (left) / 4903 (right) over $MgO+H_3BO_3$
Insufficient cohesion of MgO in spite of B_2O_3



ESL 4903 over $MgO+H_3BO_3$
Too high H_3BO_3: reaction

- Balance: ensuring cohesion / avoiding reactions

4. Flatness of LTCC

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Single LTCC sheets fired @ 875°C

- Good flatness for DP 951 and HL2000
- HL800 more problematic (needs thicker structures)

4. Flatness of LTCC with MSP

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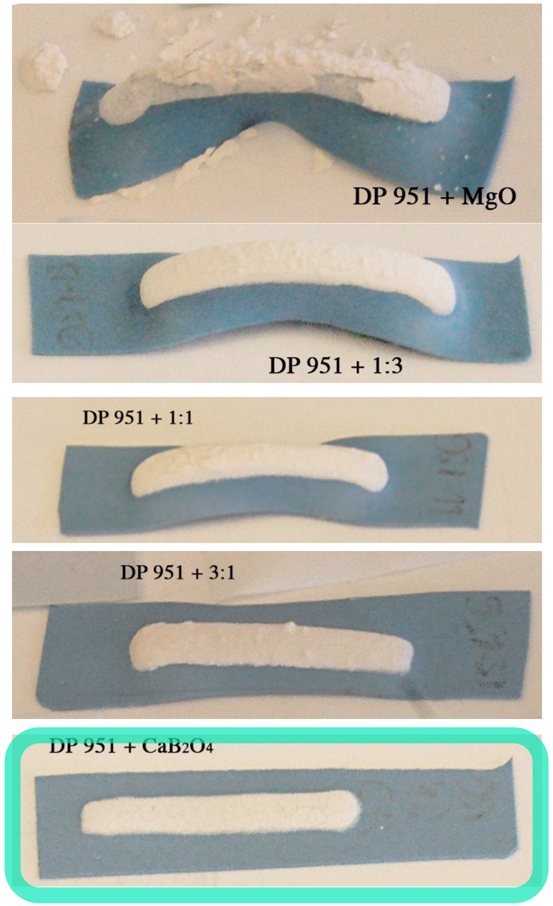
DP 951 | **HL2000**



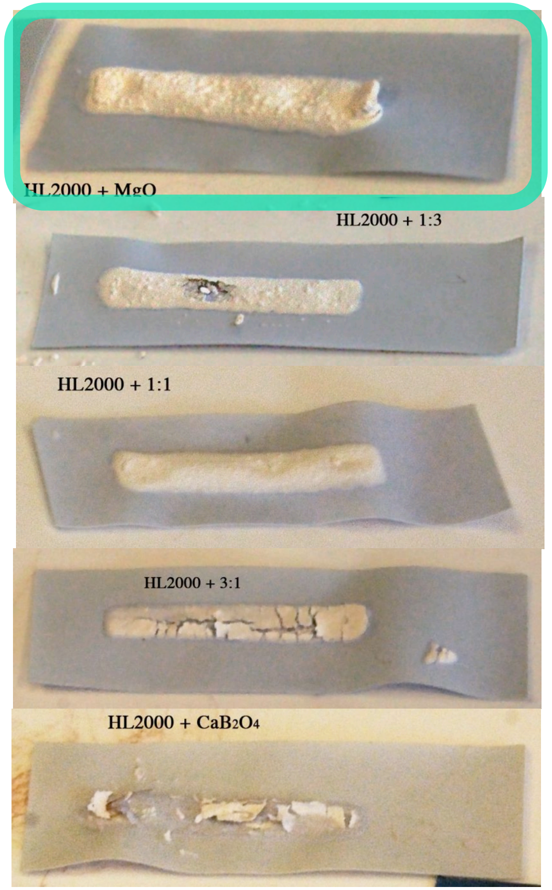
MgO

1:3

1:1

3:1

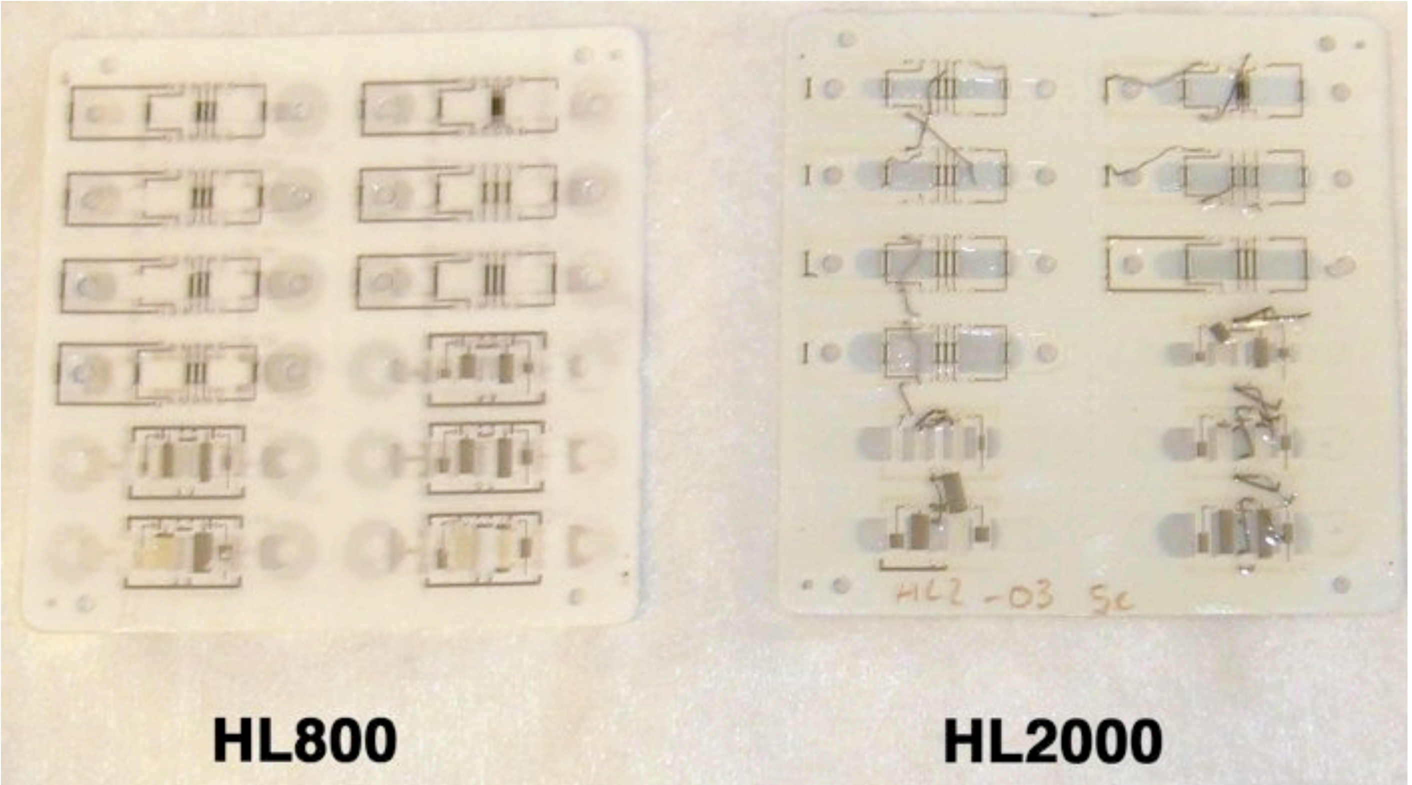
CaB_2O_4



- Expected behaviour!
- DP951 (std.) compatible with shrinkage of CaB_2O_4
- HL2000 better with MgO-rich MSPs

Deformation of LTCC + CaB_2O_4:MgO MSP mixes

4. Acid resistance of LTCC



- DP951
  - Itself : OK
  - Attacked by CaB_2O_4
- HL800: some attack
- HL2000: destroyed

4. Acid resistance of LTCC

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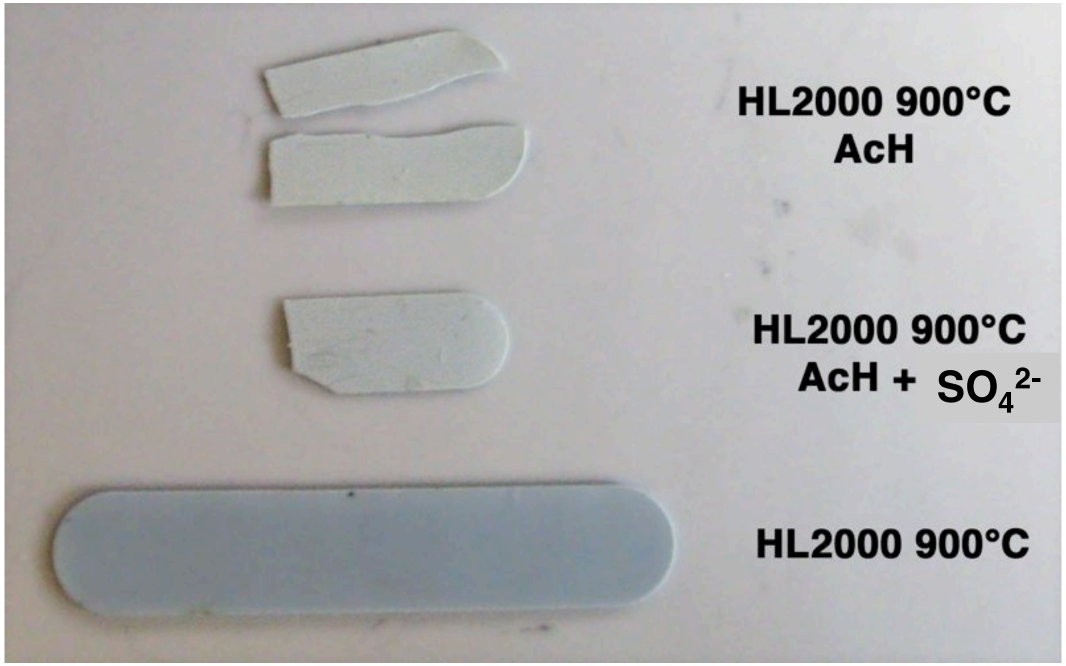

- Increase LTCC firing temperature to 900°C
- Buffering of acetic acid solution (NaAc:HAc)
- Add SO_4^{2-} ions
  - Mg soluble
  - Ca, Sr, Ba… insoluble
  - Better selectivity
  - With MgO MSP

4. Acid resistance of LTCC

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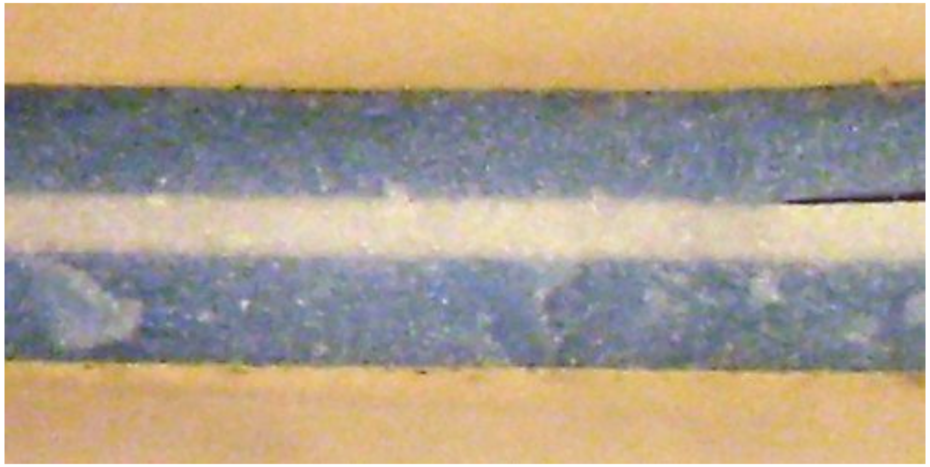

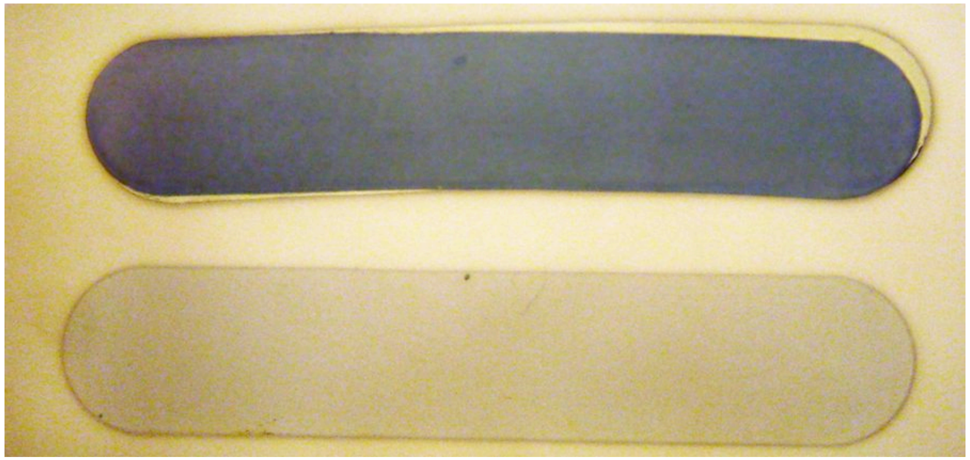

- DP951-HL-DP951 sandwich structures
- Good acid resistance
- ≈1/5 HL800 or HL2000 sufficient to block shrinkage <1%!

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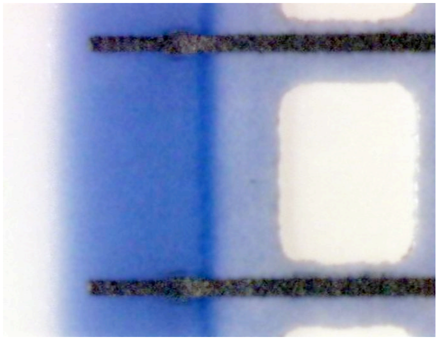
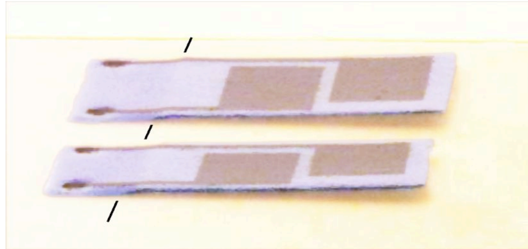
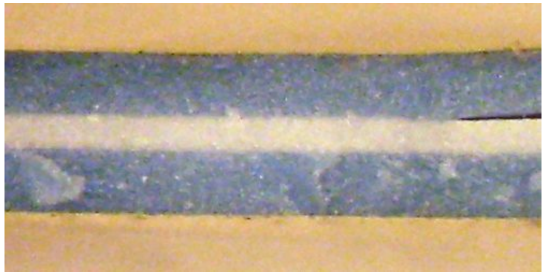
5. Conclusions

- **Thick-film : success**
  - MgO-based sacrificial layer
  - Standard firing sequence





- **LTCC : promising results**
  - Good shape stability with HL materials
  - Promising improvements in acid resistance
    - Sandwich structures with DP951
    - Optimised parameters



5. Outlook

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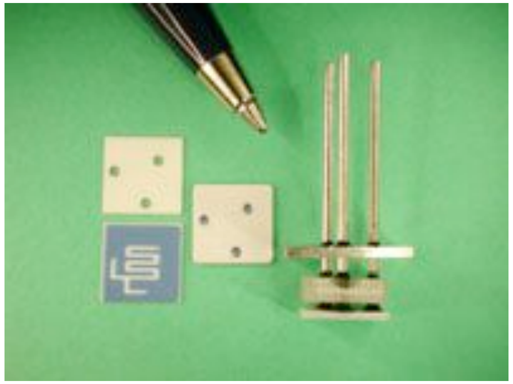
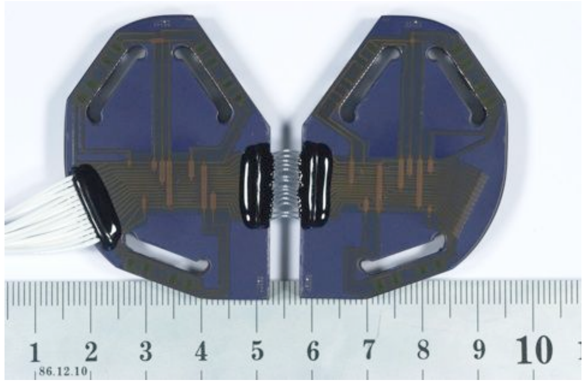
- Improve acid resistance of zero-shrink LTCC
  - Firing studies
  - Etchants with better selectivity
  - Sandwich structures where applicable

- Optimise MSPs for LTCC
  - MgO-based (soluble in sufate etchants)
  - Additives to impart limited cohesion

Merci

Thank you !