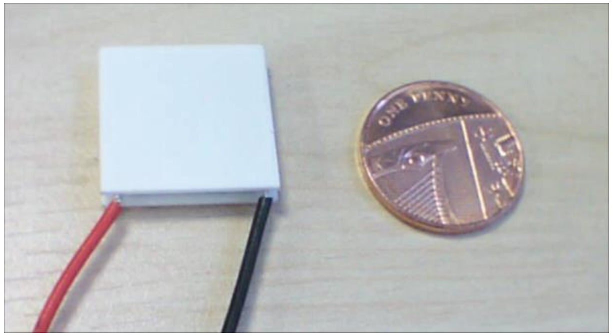
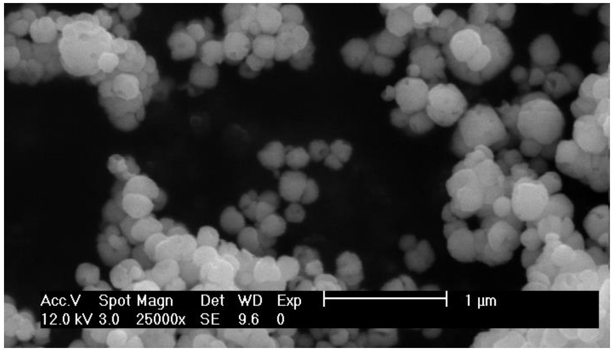
Towards manufacture of thick film thermoelectric devices

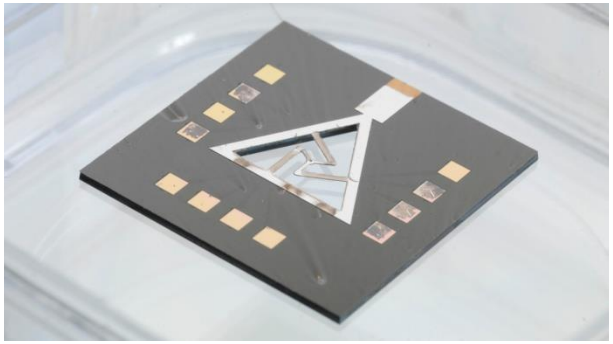
Professor Robert Dorey, Chair of Nanomaterials

Introduction

- Functional materials
- Towards sustainability through additive manufacturing for micro scale structures
- Impact on synthesis of functional materials
- Impact on processing functional additively manufactured structures







ENHANCED

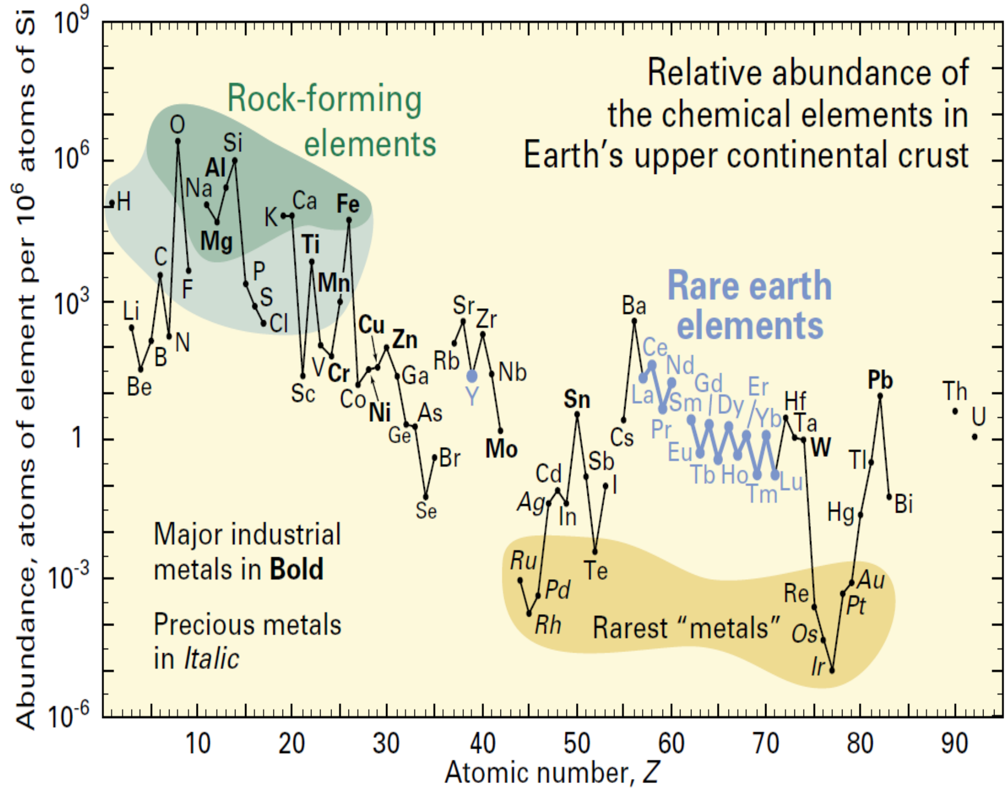
MASSIVE Functional Materials

Innovate UK
Technology Strategy Board

EPSRC

Environmentally safe and sustainable functional materials

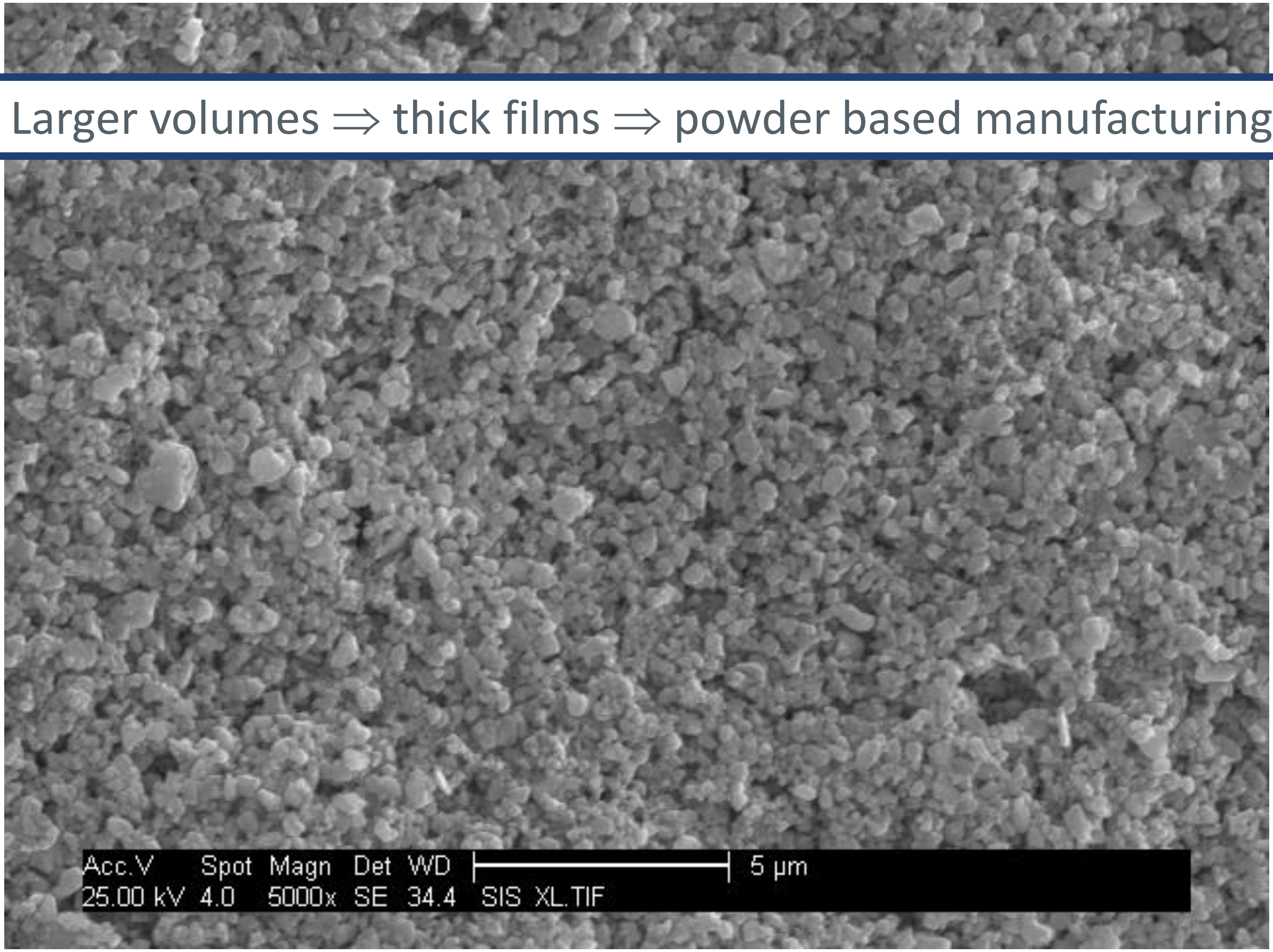
	Commercial materials	Potential alternative materials
Thermo electrics	**SbTe, BiTe,** PbTe, SiGe	**$NaCo_2O_4$,** Mg_2Si, $MnSi_x$, $SrTiO_3$, BiSrCoO, FeS, Bi_2S_3, Cu_xS, TiS_2, ZnO,
Piezo/Pyro/ Ferro/Di- electrics	$Pb(Zr,Ti)O_3$, $PbTiO_3$, $PbMgNbO_3$	$(K,Na)NbO_3$, $(Bi,Na)TiO_3$, $LiNbO_3$
Electrode and interconnect structures found in all devices	Pt, Pd, InSnO (ITO), Ni	Al-ZnO, TiN, Y-$SrTiO_3$, La-$SrTiO_3$



ENHANCED MASSIVE Functional Materials

Powder based films

Power ⇒ Larger volumes ⇒ thick films ⇒ powder based manufacturing

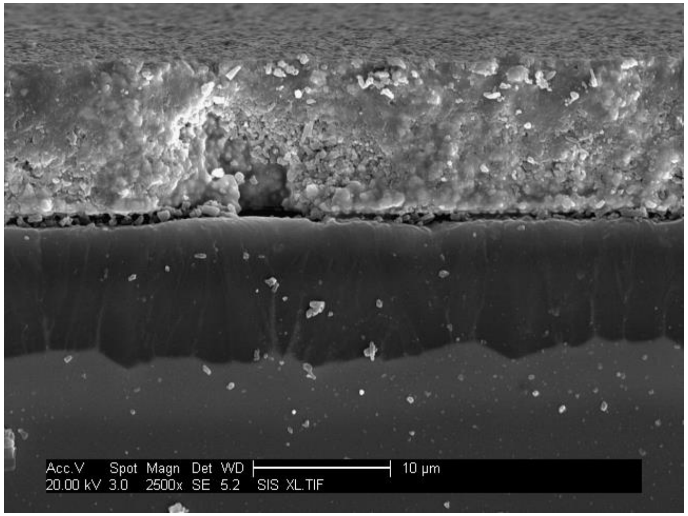


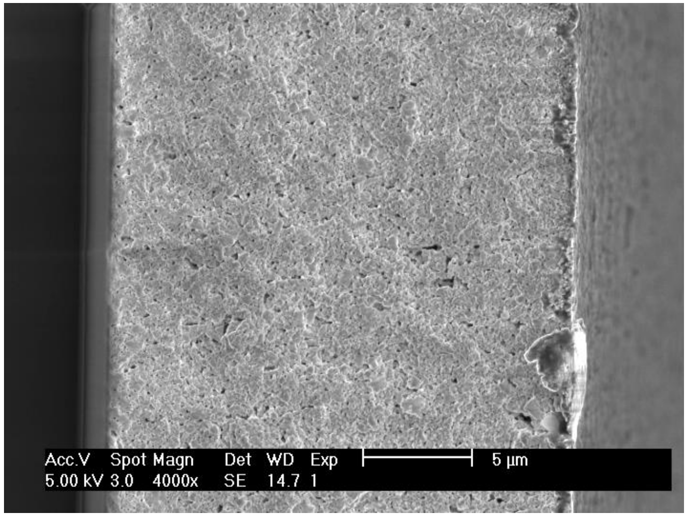
PZT film before sintering

Co-processing

Temperature induced degradation:
- Interdiffusion
- **Evaporation**
- Degradation

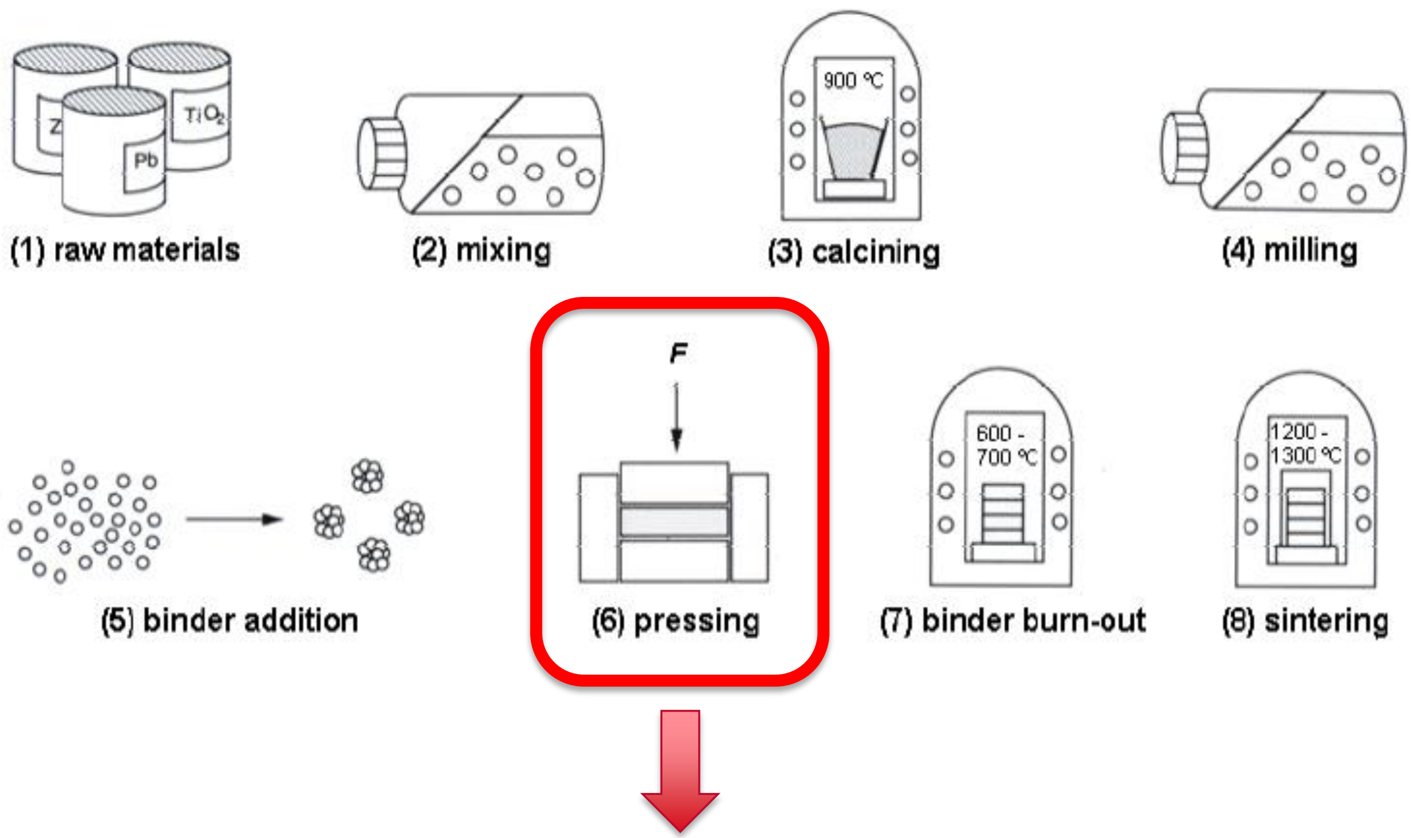
Solutions:
- Low temperature
  e.g. Compsite sol gel < 750°C for PZT/Si
- Diffusion barrier e.g. ZrO_2





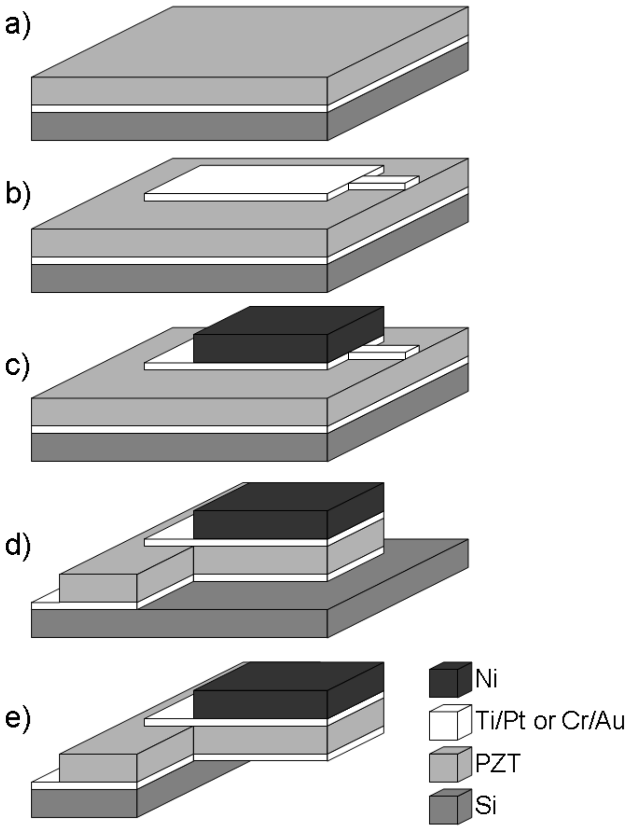
R.A. Dorey, S.B. Stringfellow, R.W. Whatmore, Effect of sintering aid and repeated sol infiltrations on the dielectric and piezoelectric properties of a PZT composite thick film, J.Euro.Ceram.Soc., 22, 2921-2926, 2002.

Manufacturing

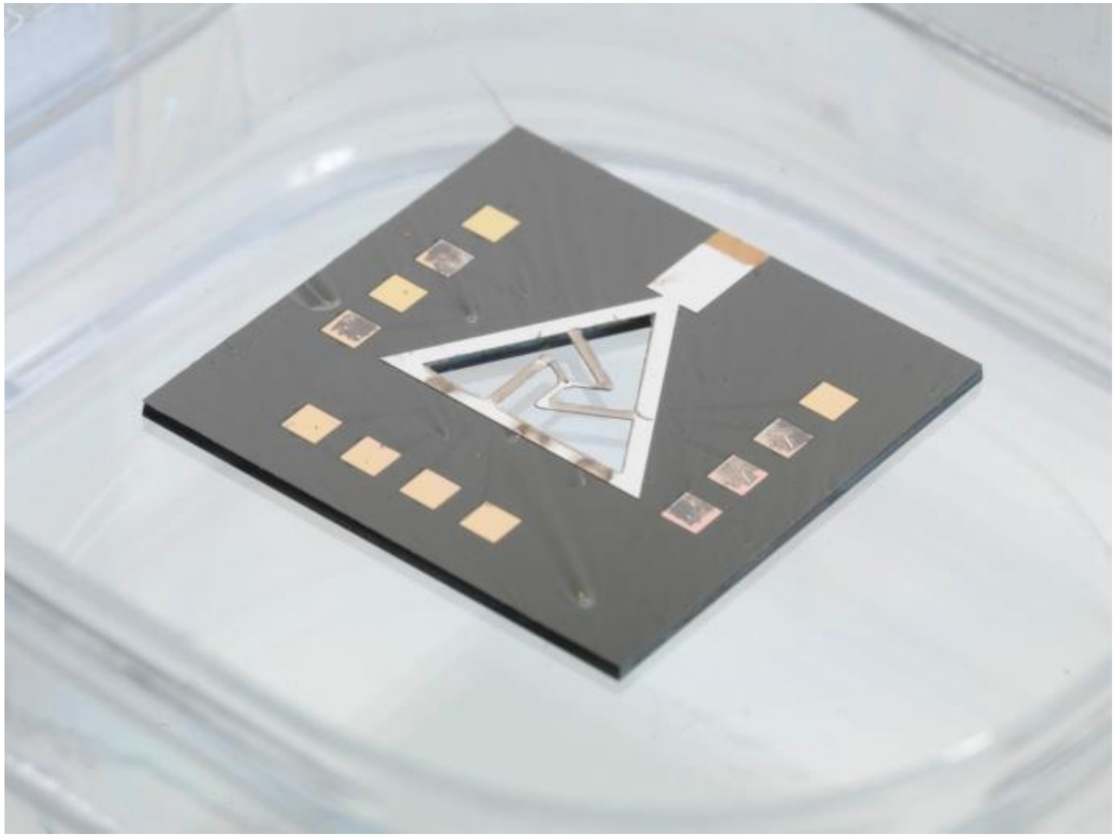


Additive manufacturing techniques

Manufacture of film based devices

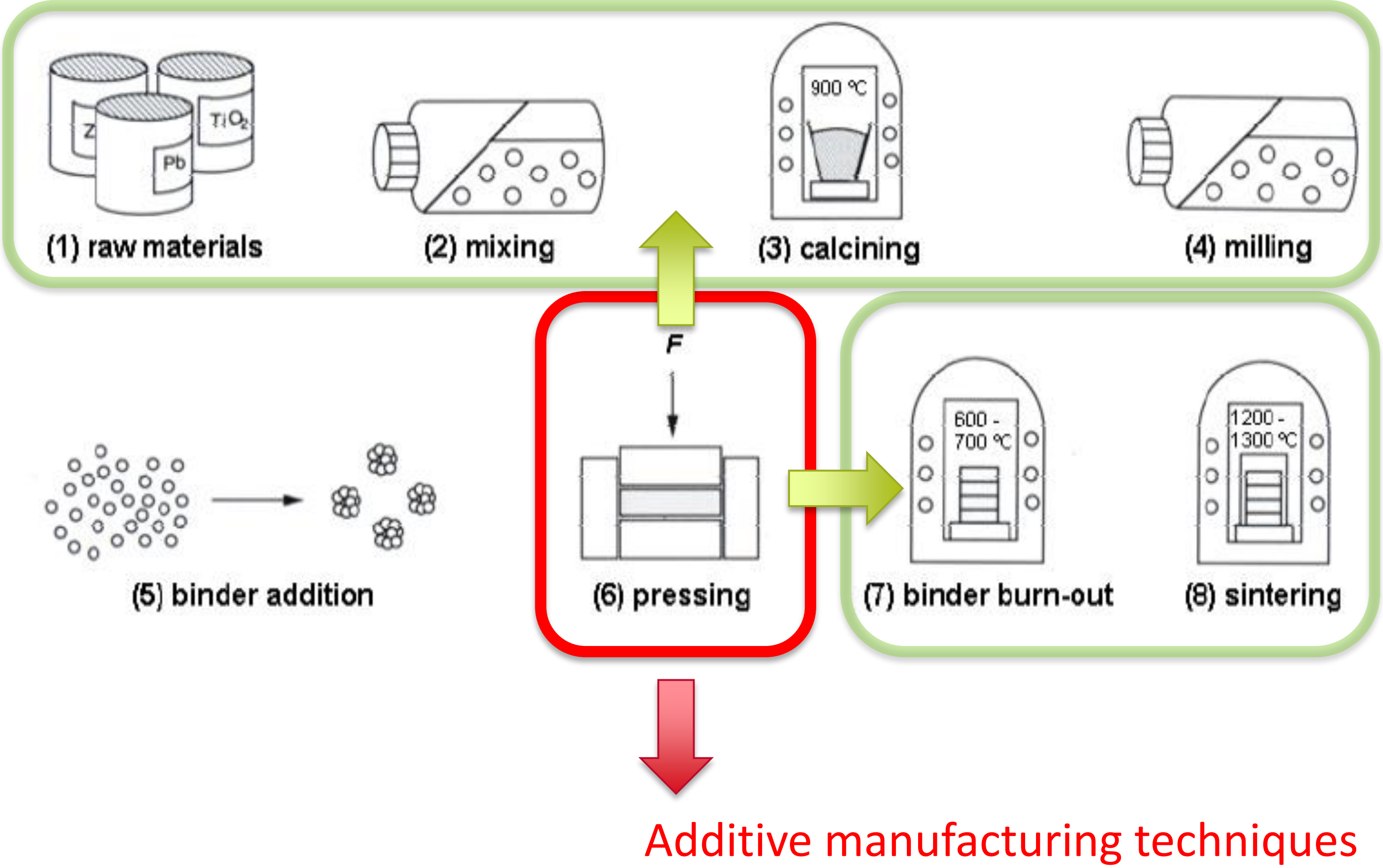


Fabrication stages



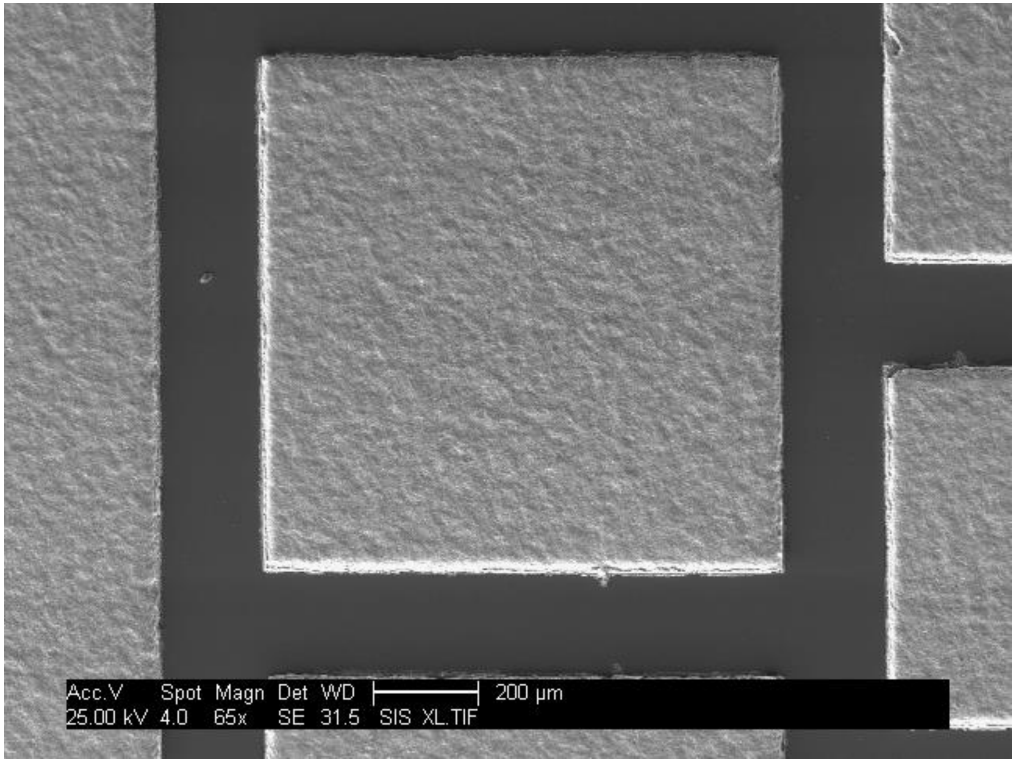
Micro coordinate measurement tool sensor/actuator

Additive manufacturing: knock-on effects

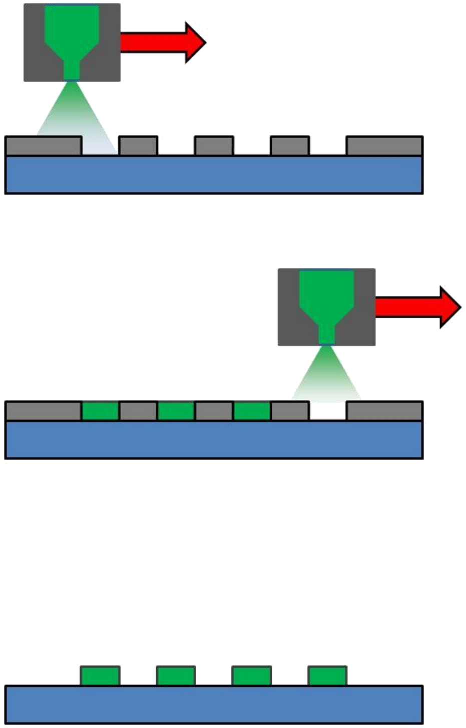


Additive manufacturing techniques for structured films

Structuring – micromoulding

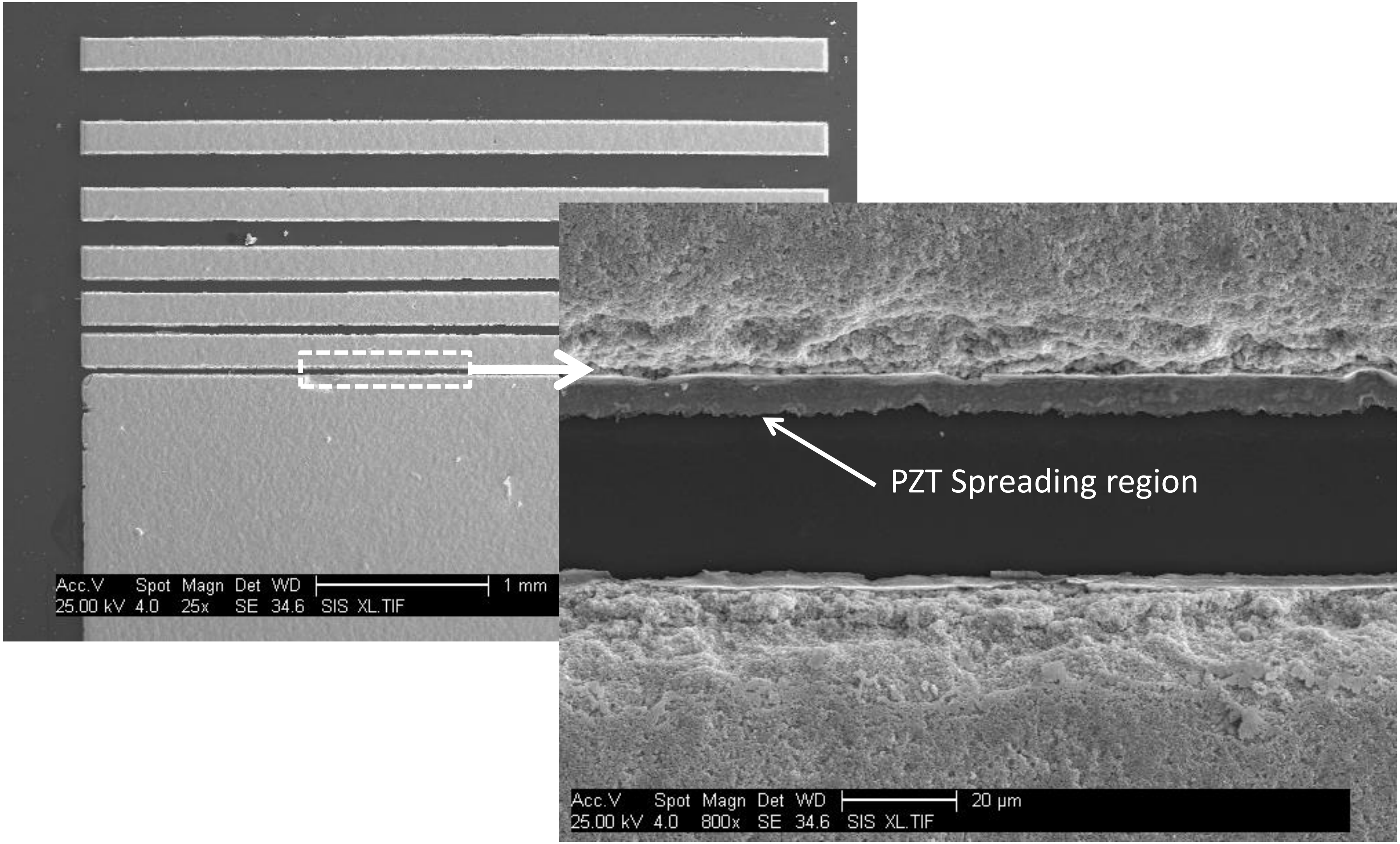


PZT features created by micro moulding

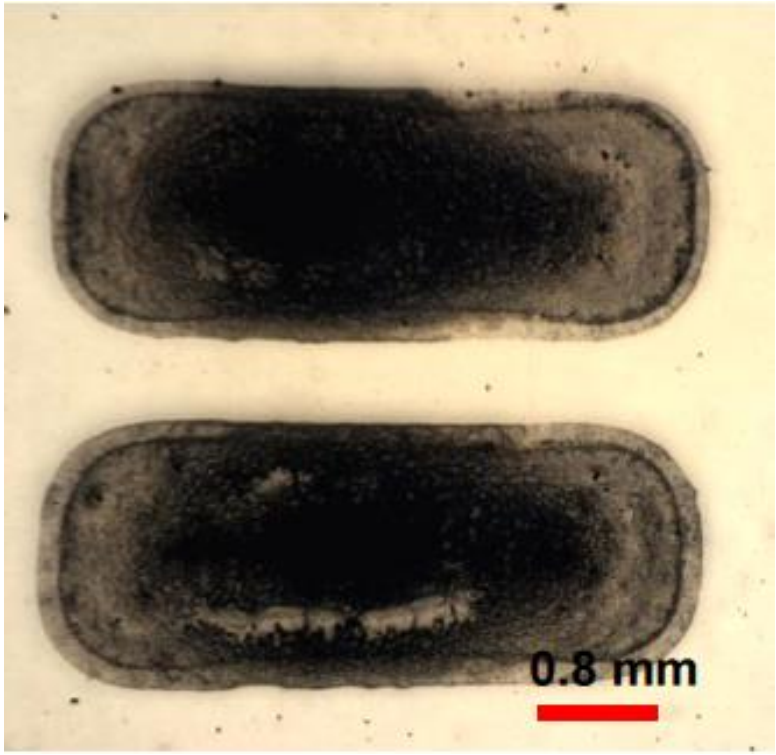


D. Wang, S.A. Rocks, R.A. Dorey, Micromoulding of PZT film structures using electrohydrodynamic atomization mould filling, J.Euro.Ceram.Soc., 29, 1147–1155, 2009. .

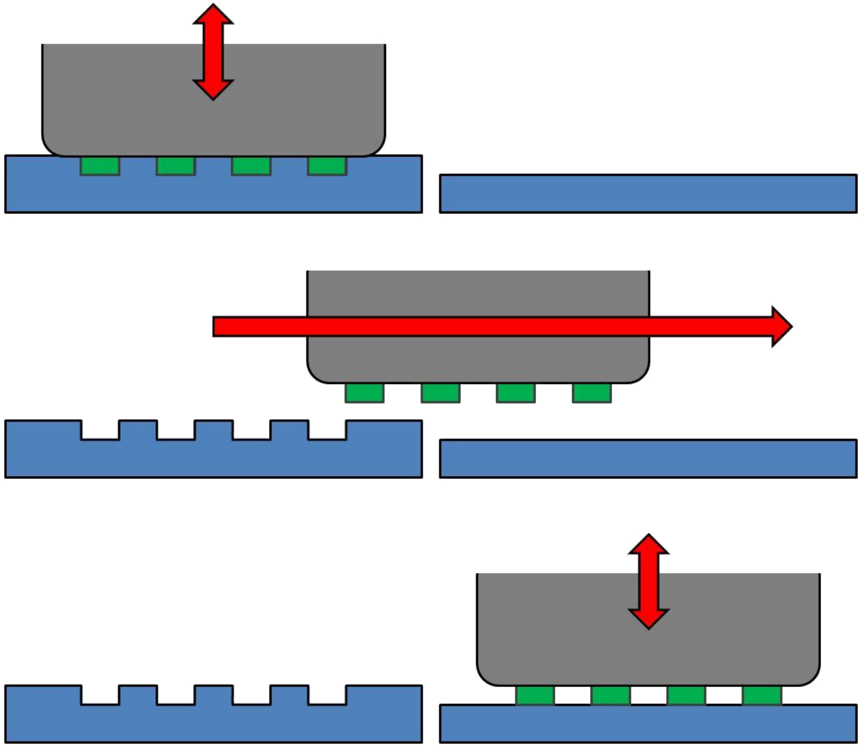
Structuring – micromoulding



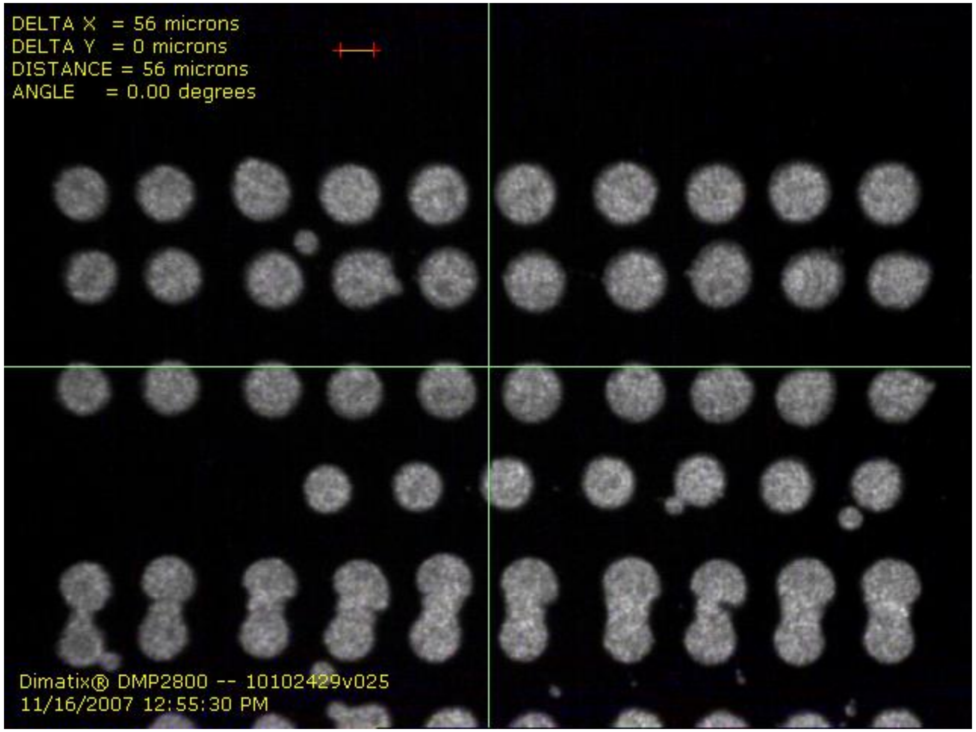
Structuring – pad printing



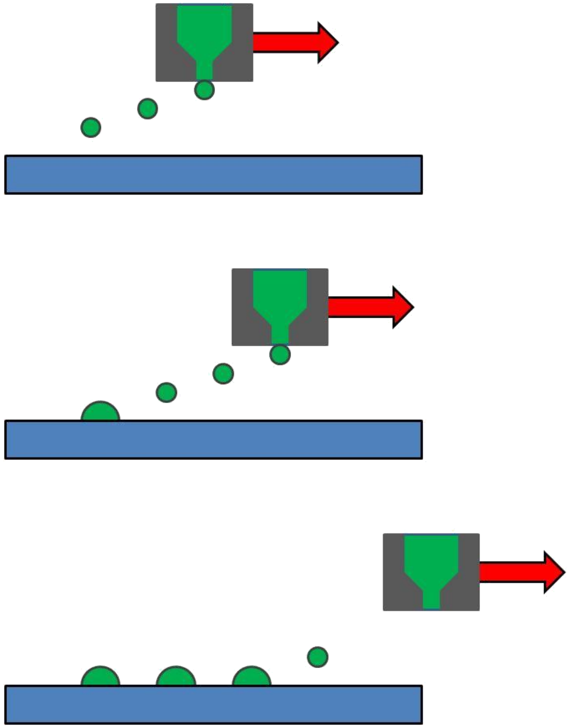
Silver NPs deposited by pad printing



Structuring – direct writing



PZT features created by ink jet printing



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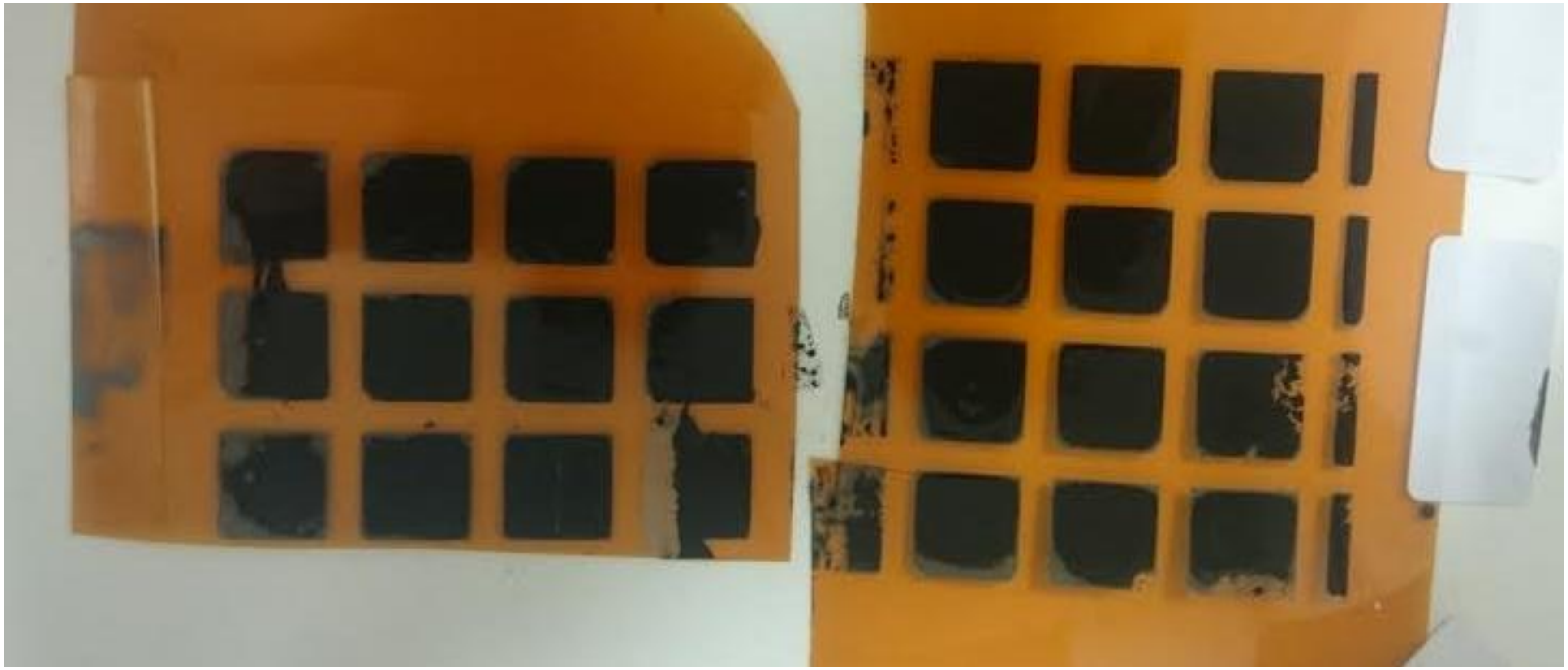
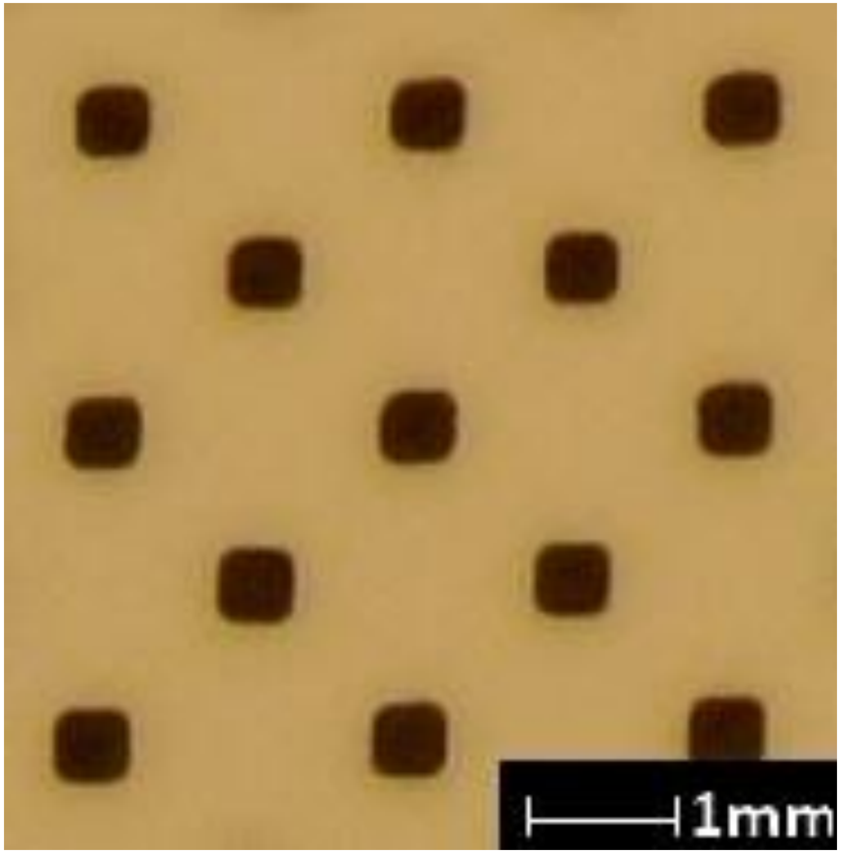
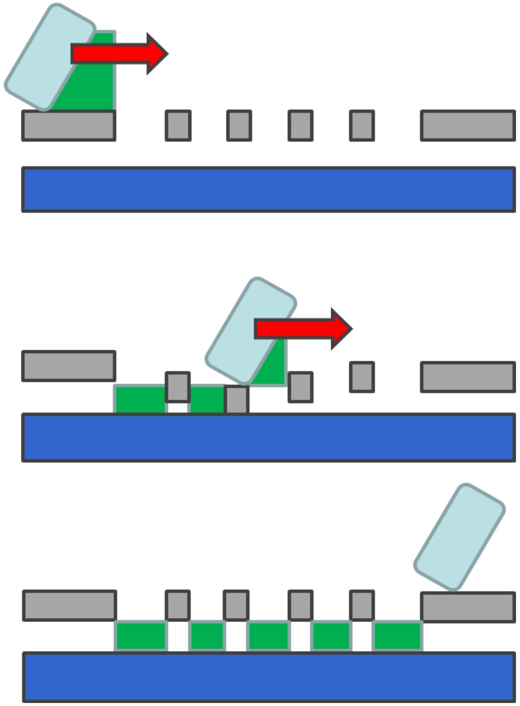


Bi2Te3 features created by ink jet printing an aqueous ink

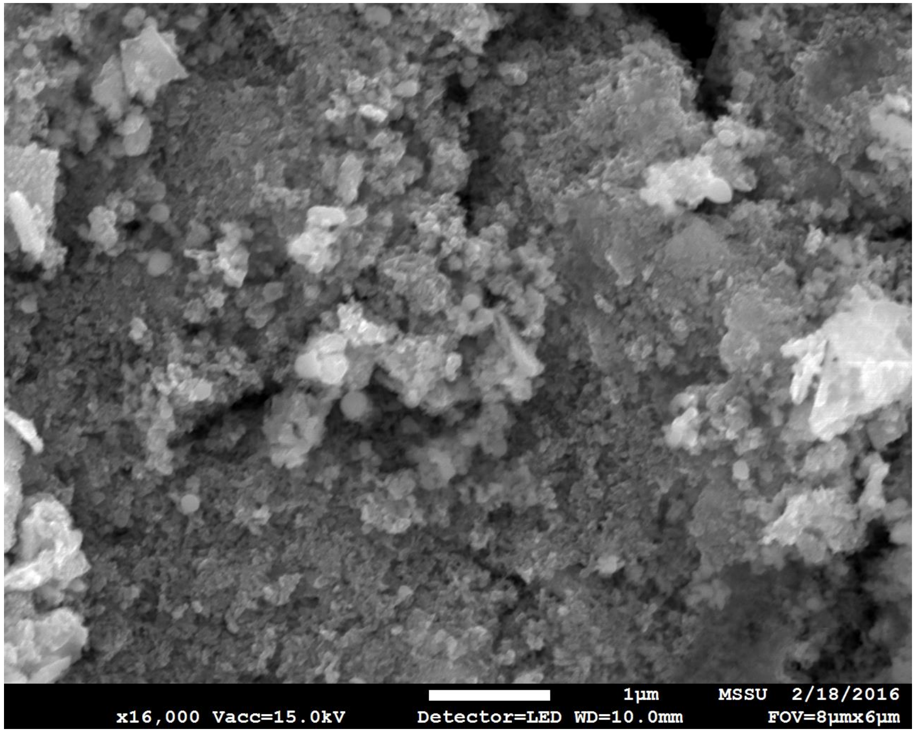
Deposition – screen printing



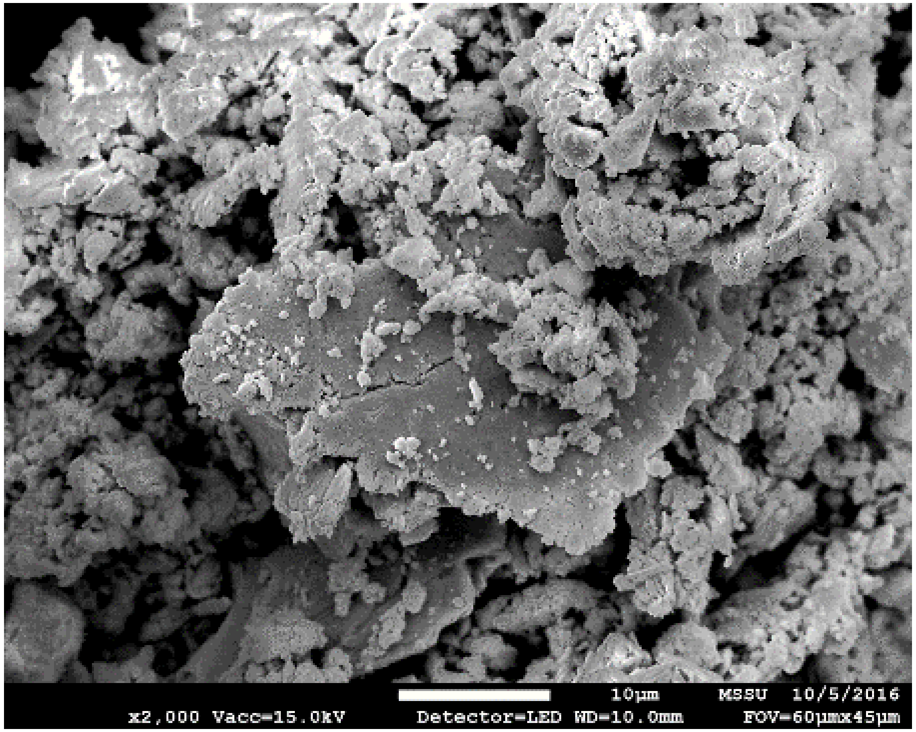
Bi_2Te_3 features created by screen printing



Structuring – direct writing

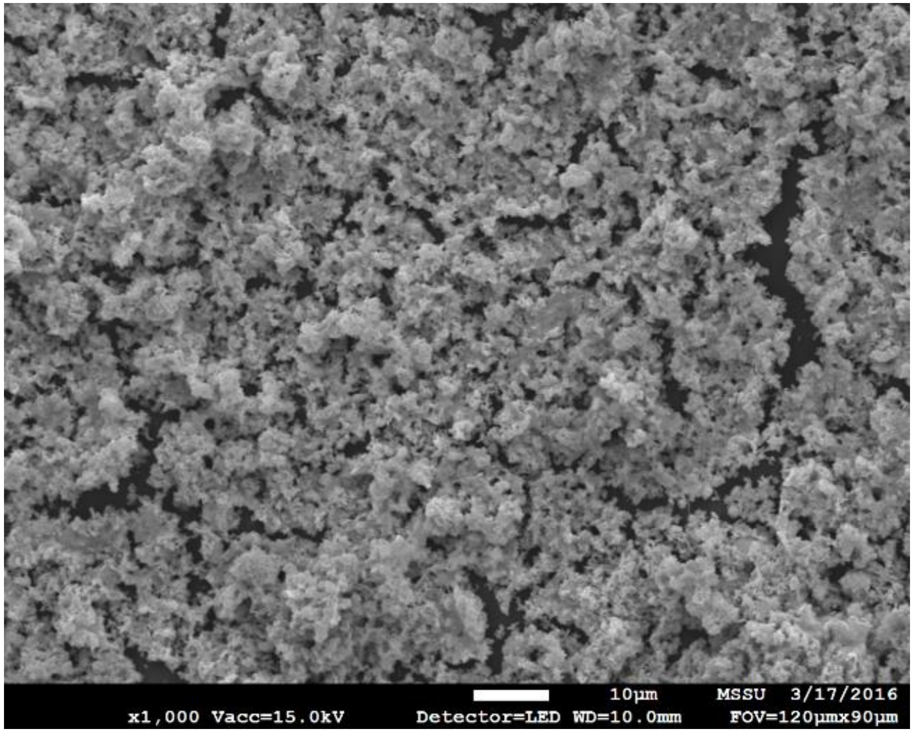


Bi_2Te_3 powder prepared for ink jet printing

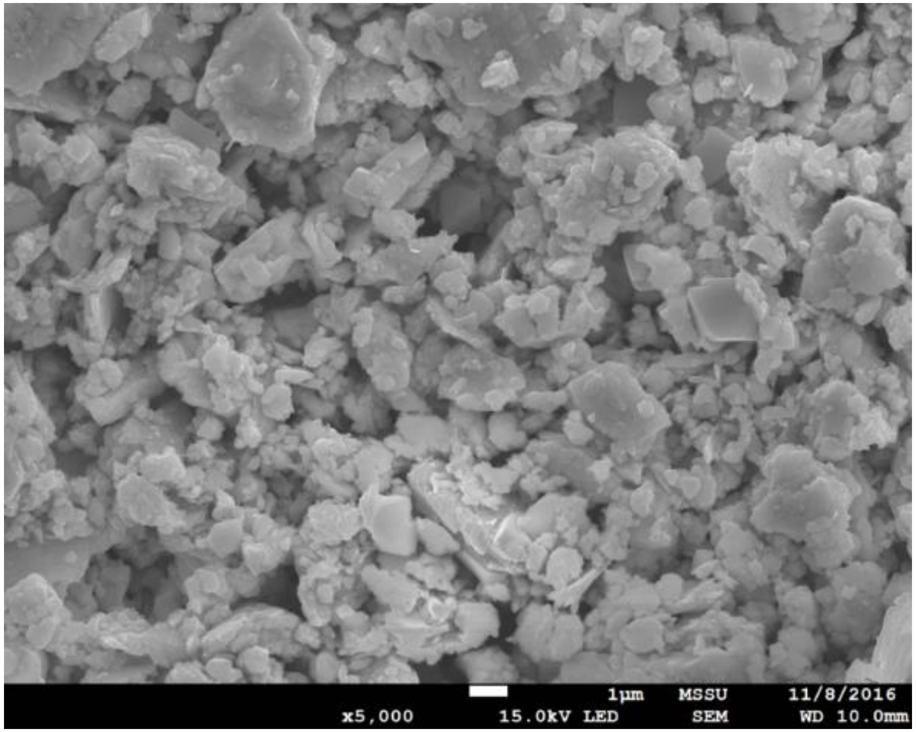


Sb_2Te_3 powder prepared for screen printing

Structuring – direct writing



Ink jet printed Bi_2Te_3



screen printed Sb_2Te_3

Additive manufacturing techniques for structured films

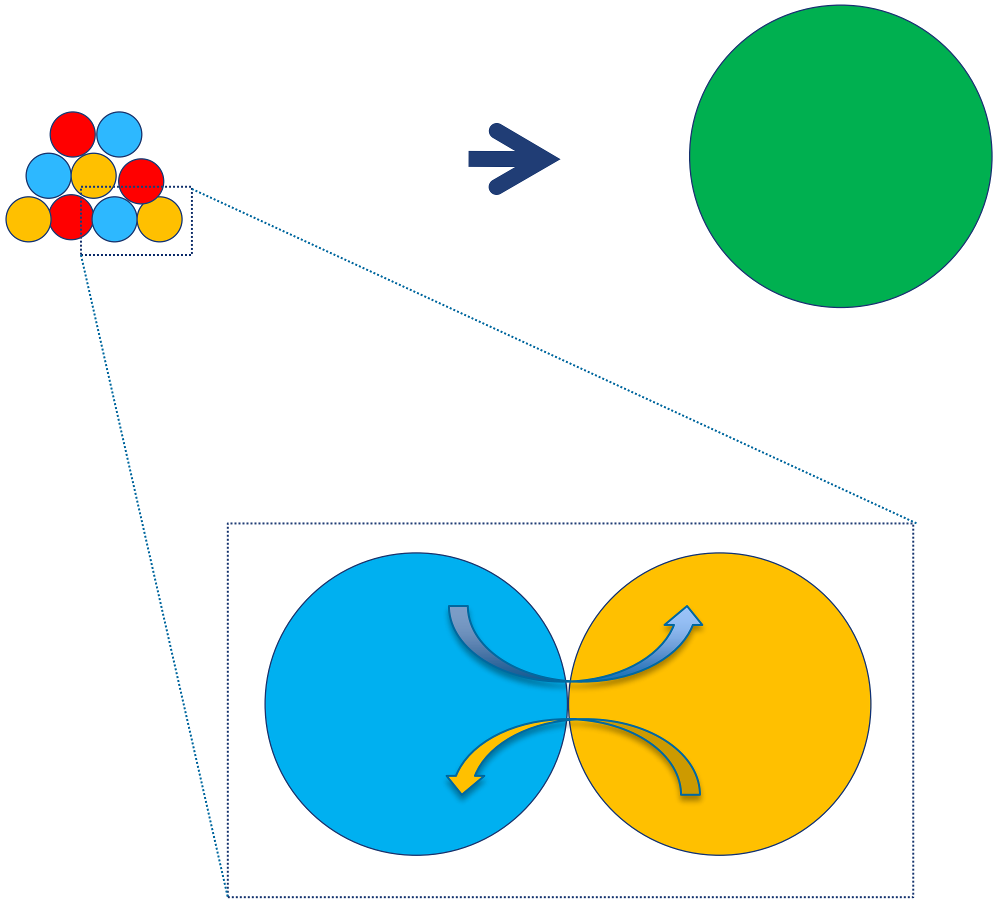
Design criteria

Building block size << feature size

Powder synthesis

Need small functional (multi-element) materials particles

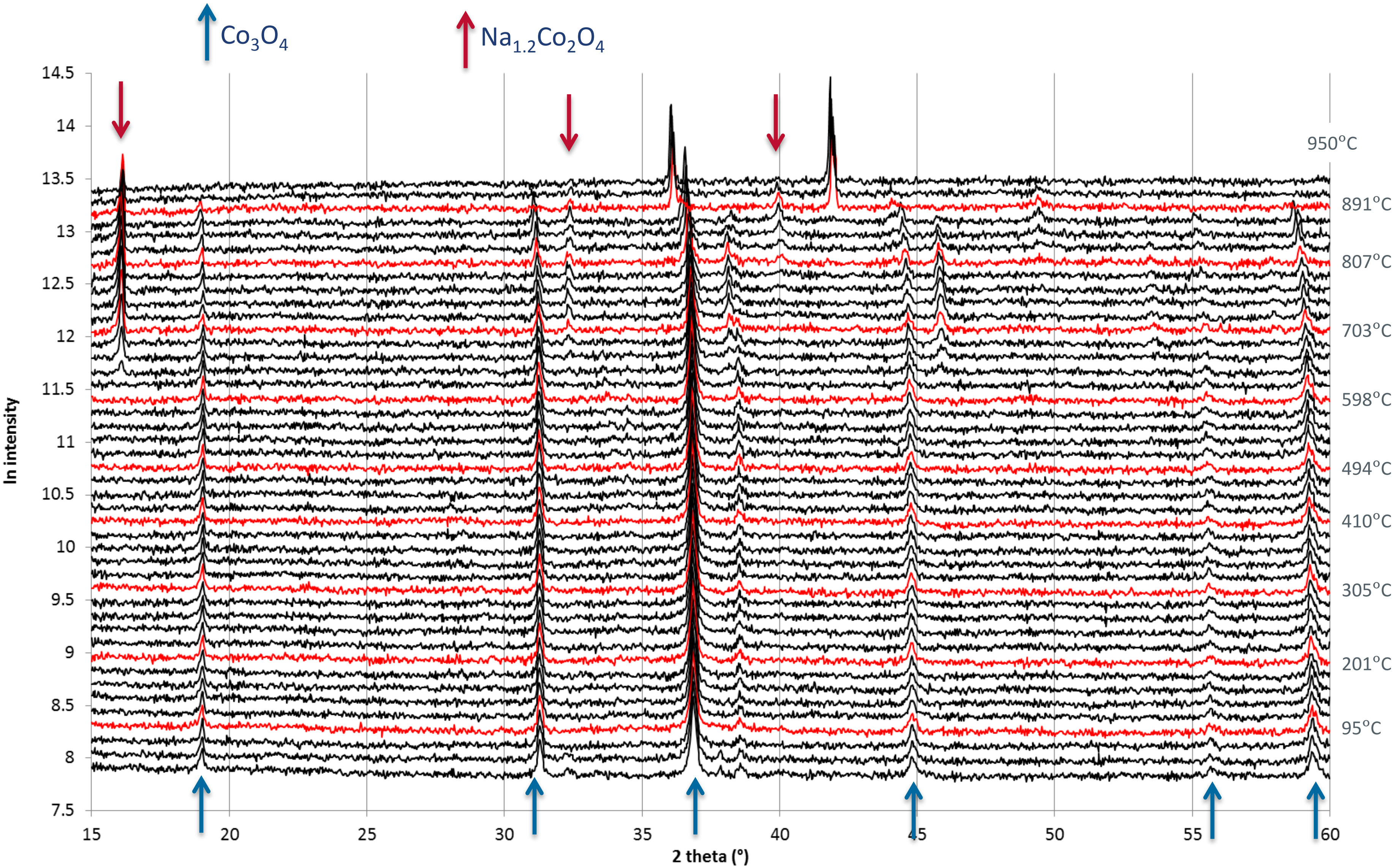
Fusion based techniques #1: particle growth



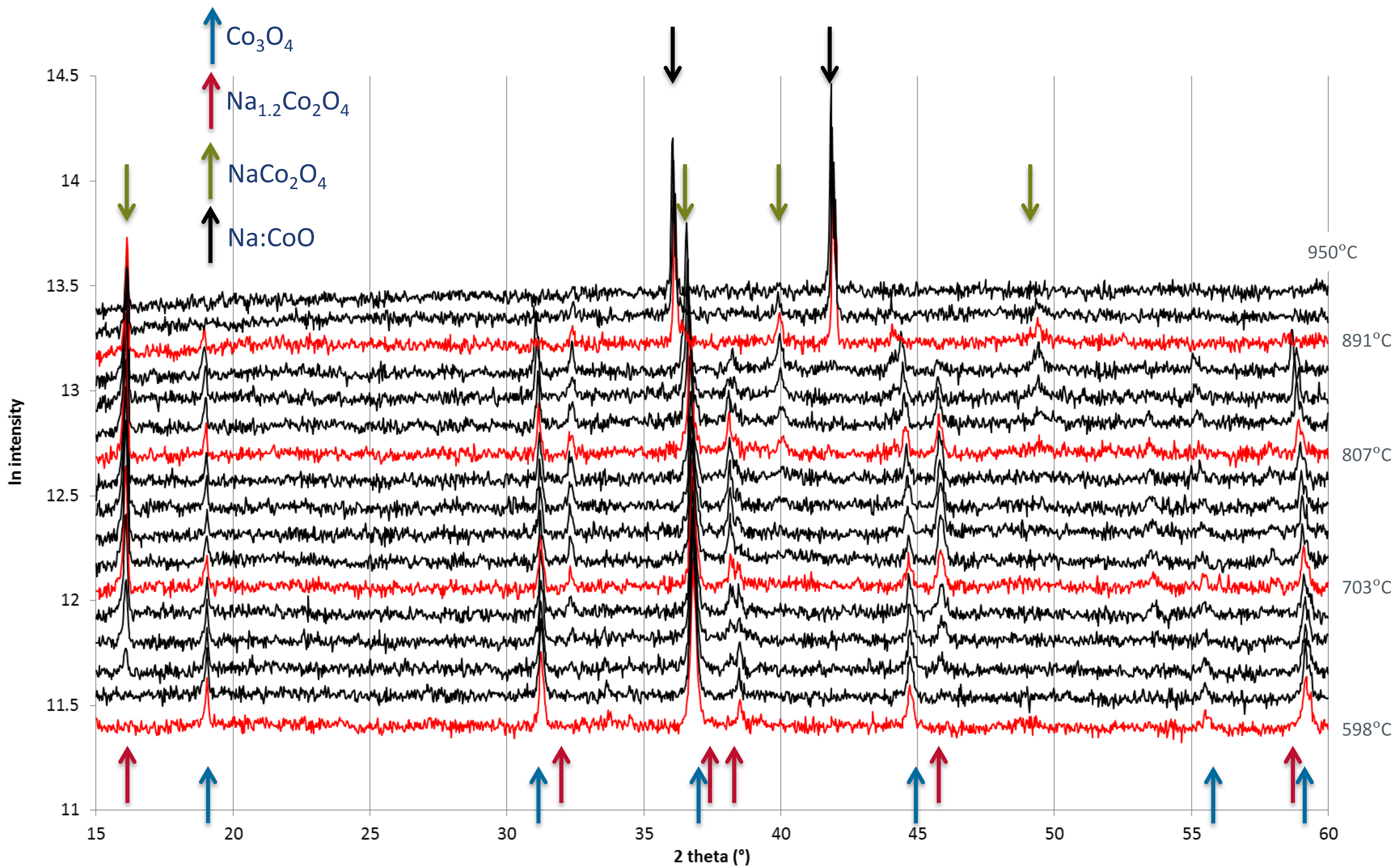
Particle growth due to coalescence of multiple primary particles

= Fundamental limit on particle size

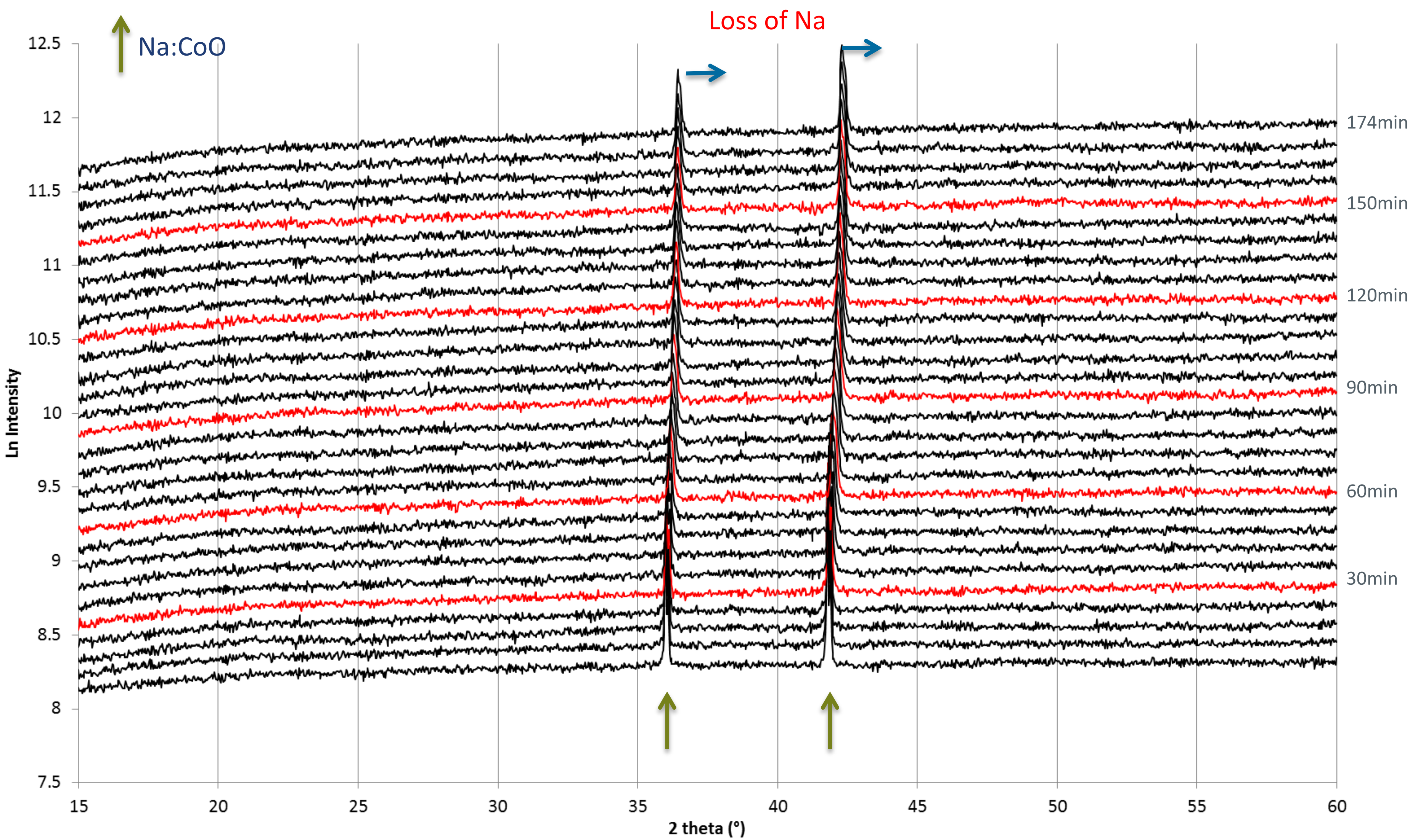
Fusion based techniques #2: phase evolution



Fusion based techniques #2: phase evolution



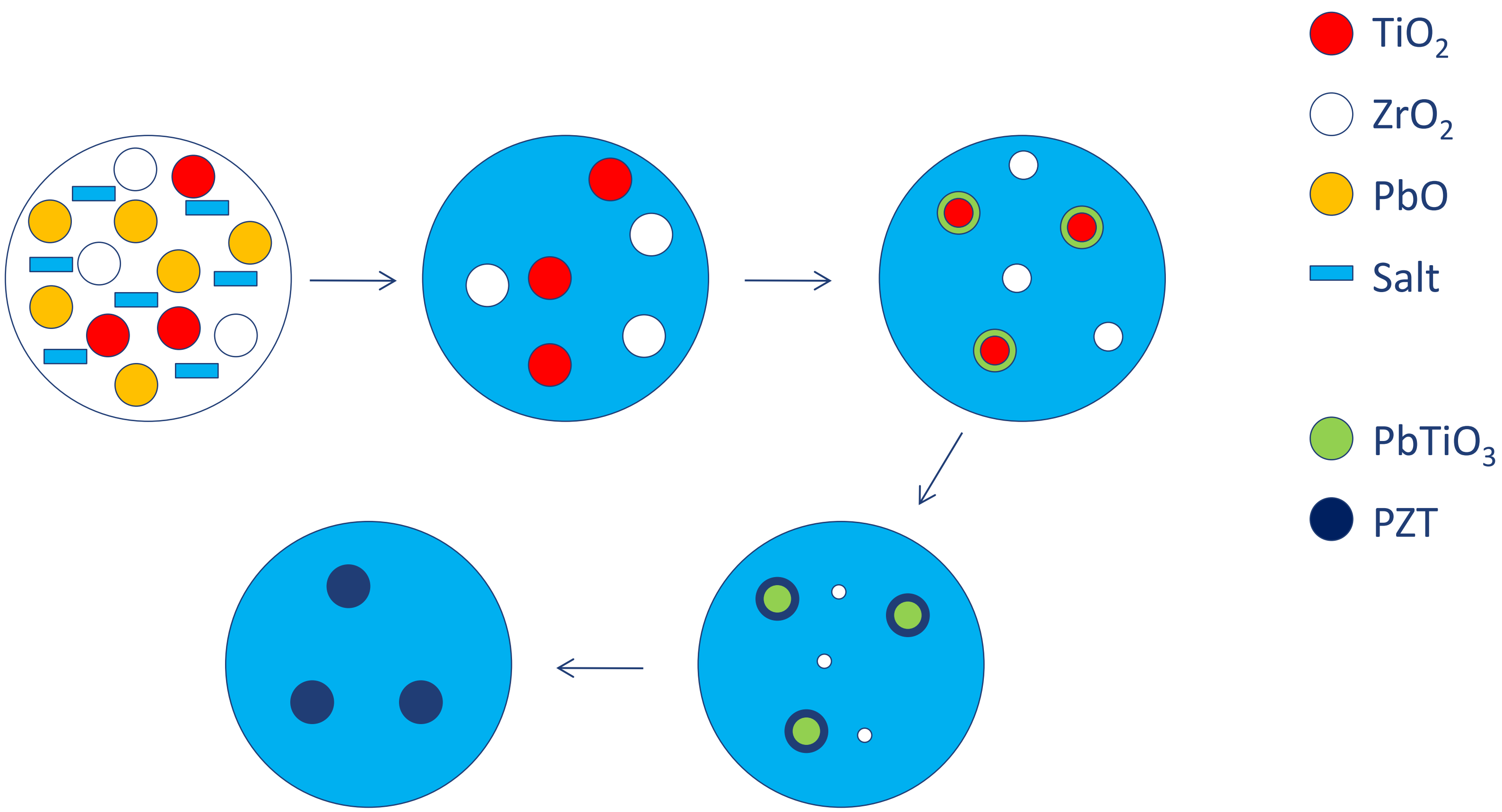
Fusion based techniques #2: phase evolution (950°C hold)



Powder synthesis

Liquid phase/bottom up required

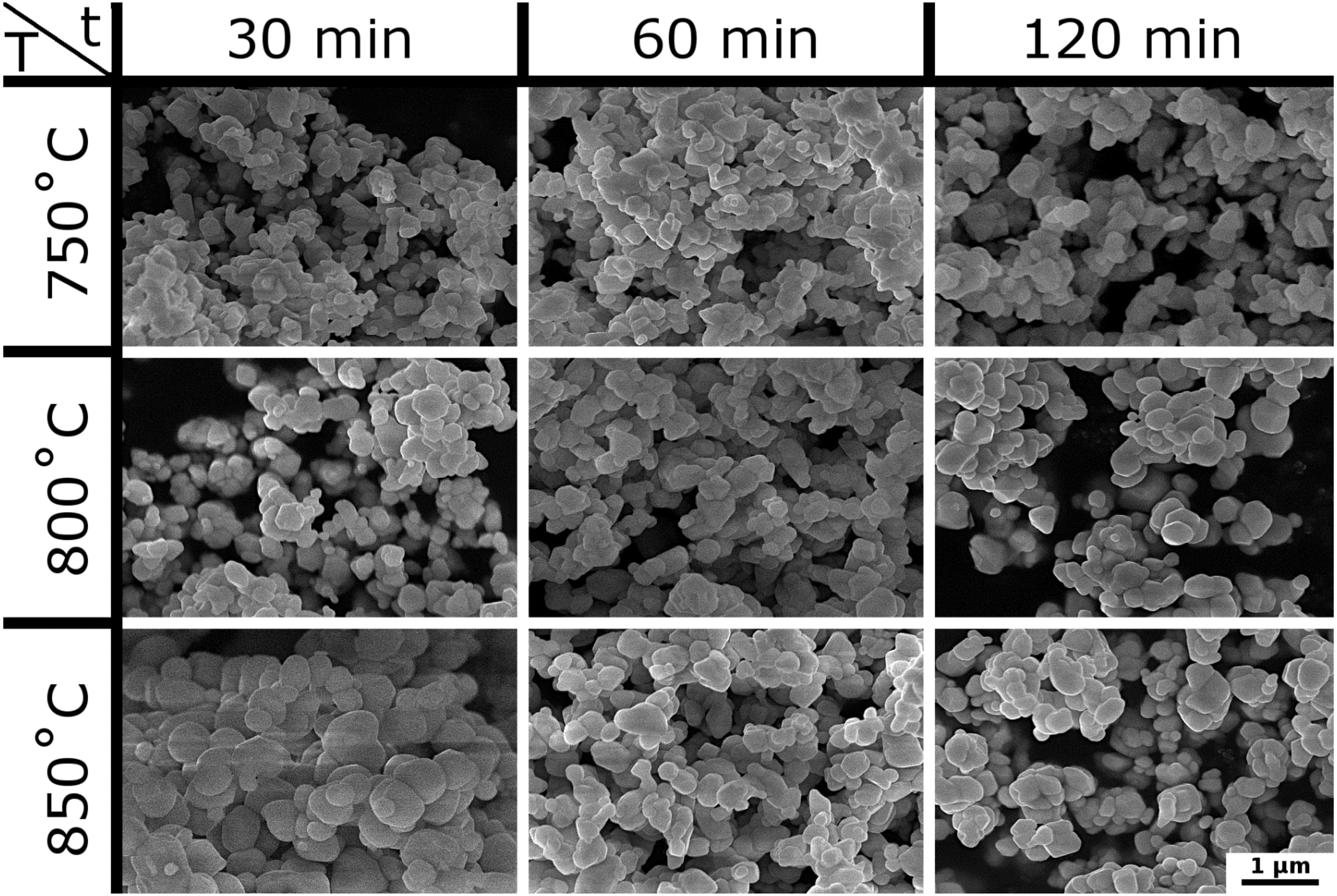
Molten salt synthesis



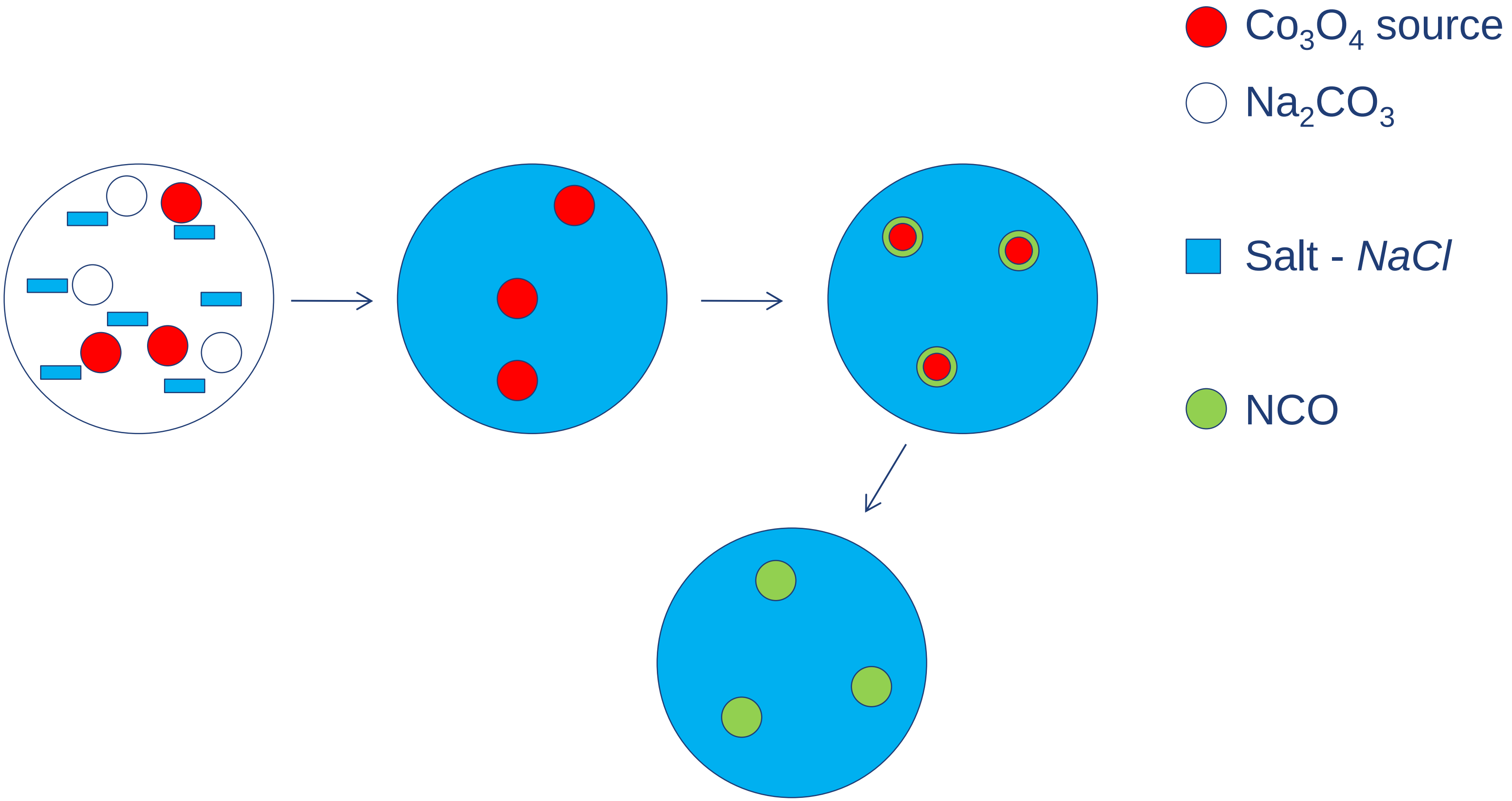
PbO soluble in NaCl/KCL – ZrO_2 slight solubility

F. Bortolani, R.A.Dorey, Molten salt synthesis of PZT powder for direct write inks, J. Euro.Ceram.Soc., 30, 2073-2079, 2010

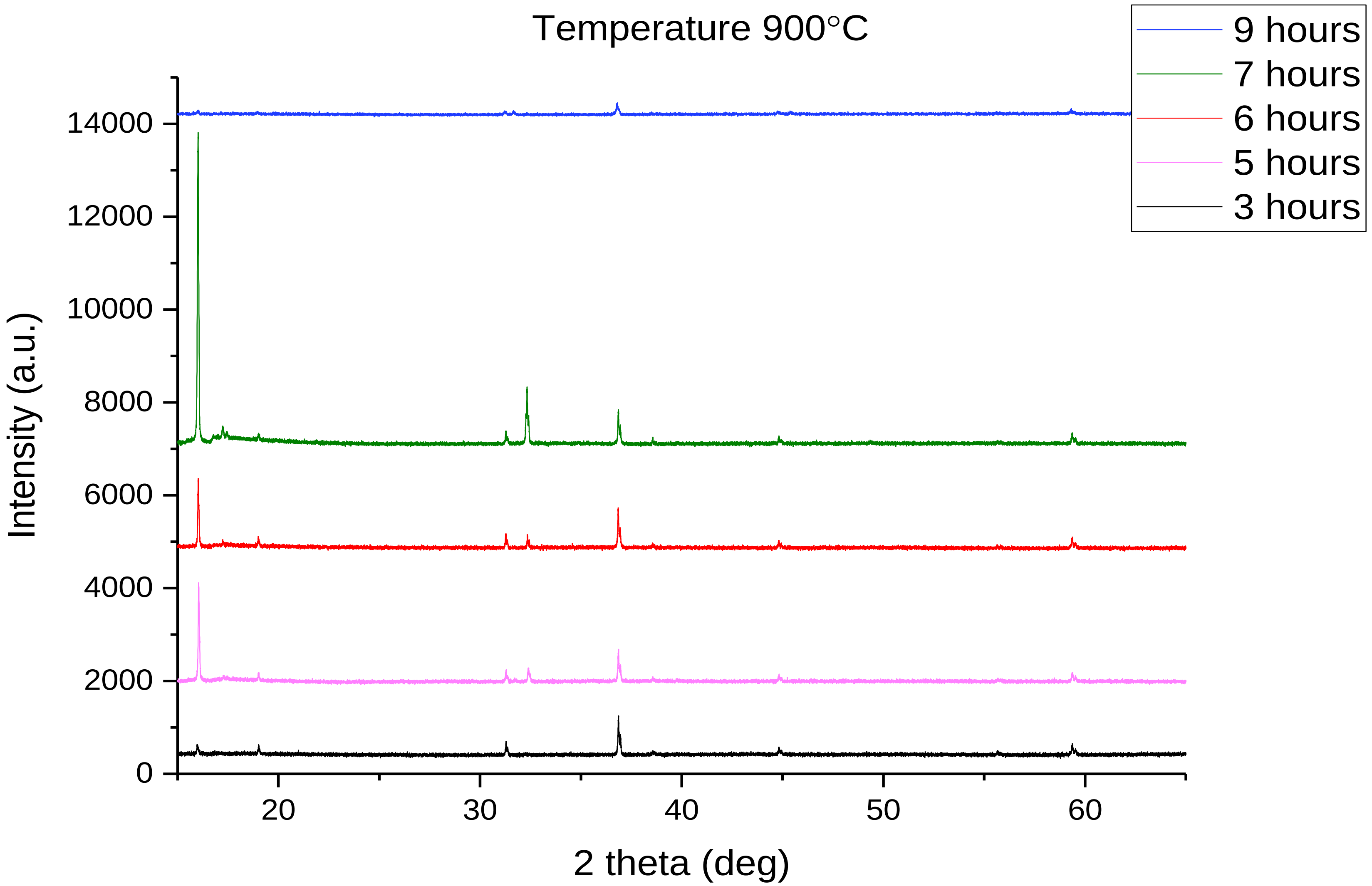
Molten salt synthesis



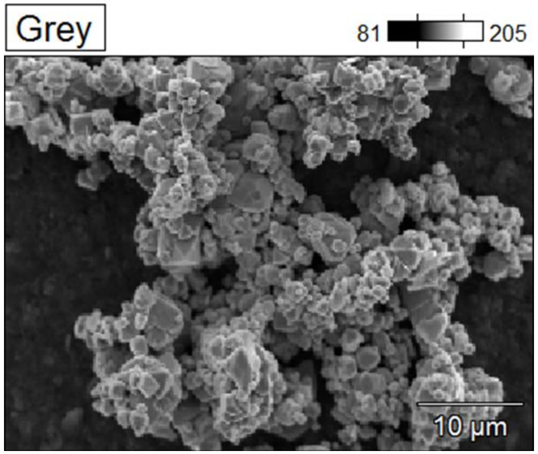
Molten salt synthesis – $NaCo_2O_4$



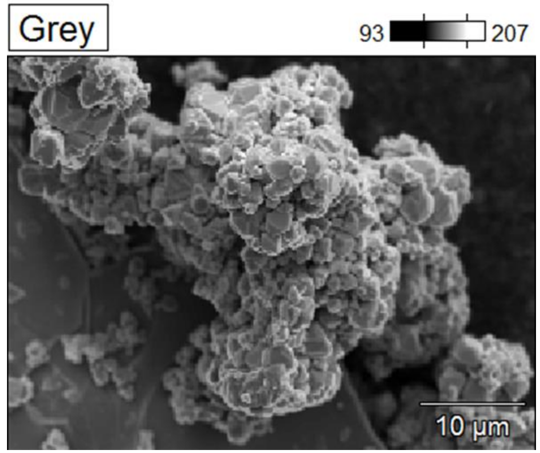
$NaCo_xO_y$ evolution (MSS@900°C)



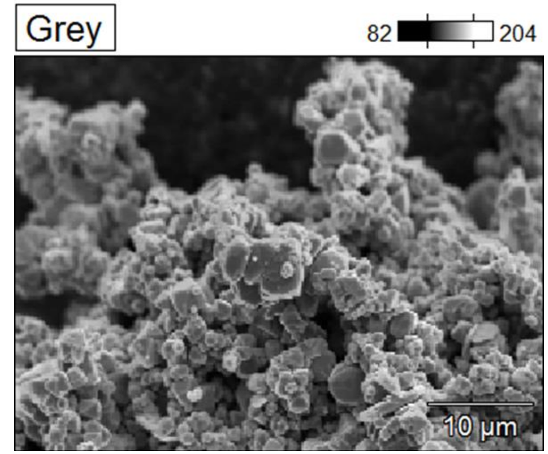
$NaCo_xO_y$ evolution (MSS@900°C)



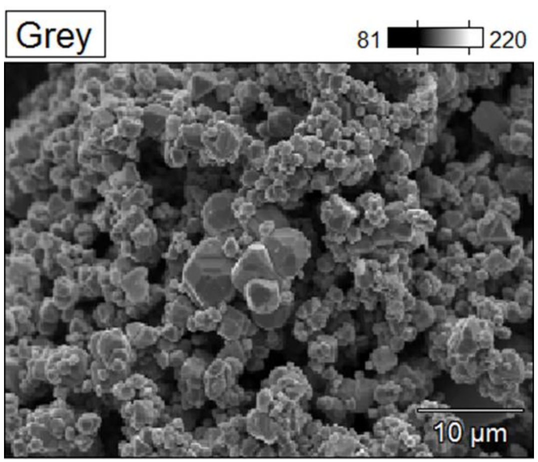
3h



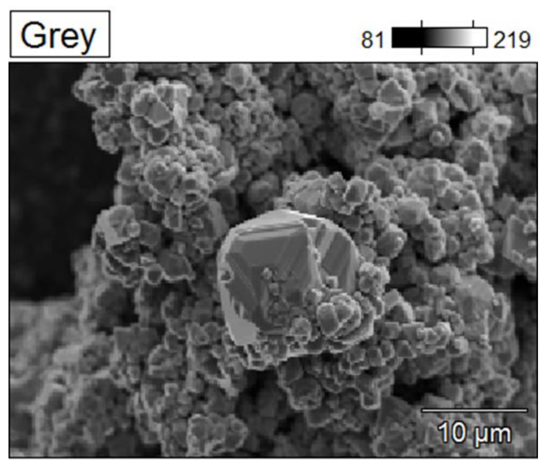
5h



6h



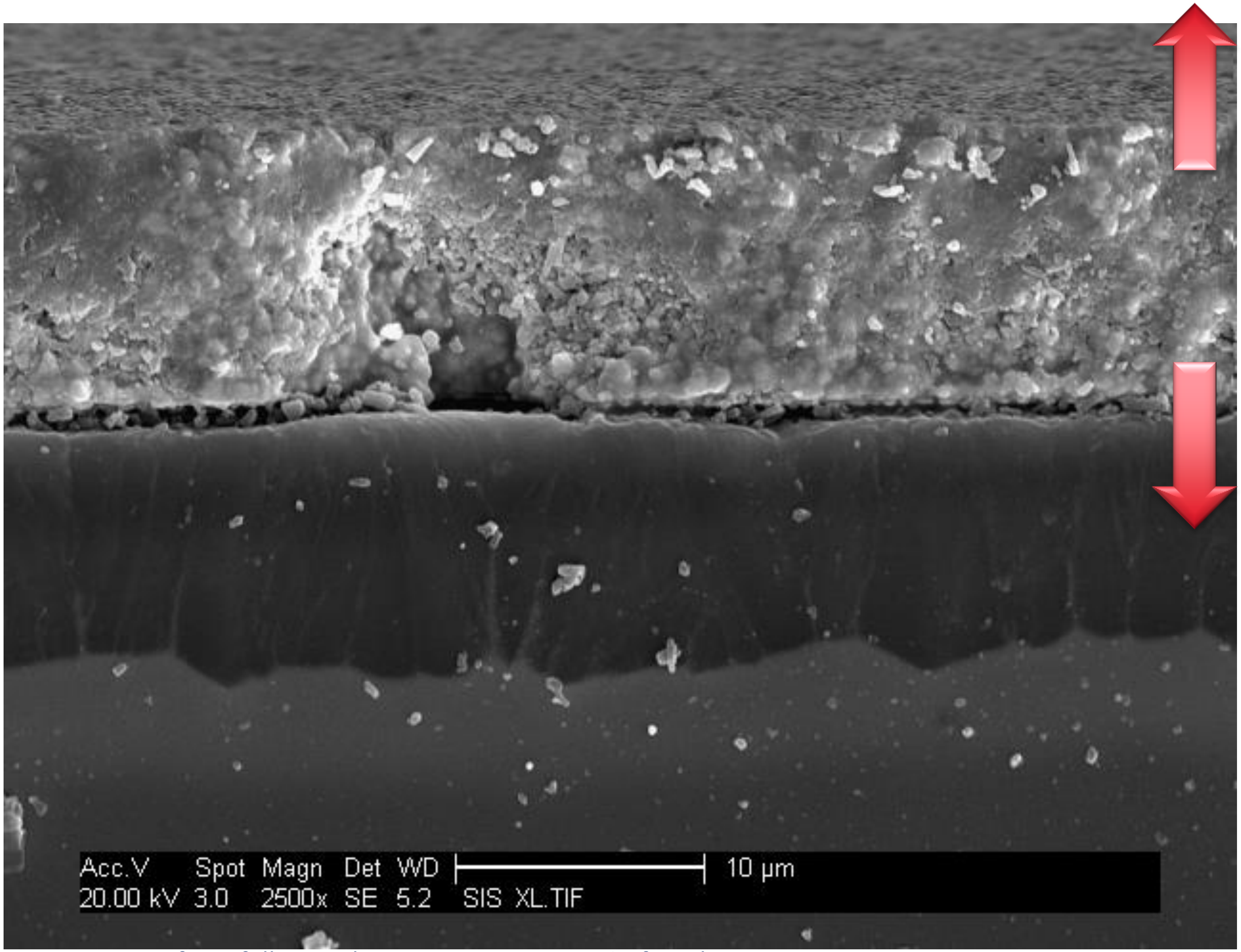
7h



9h

Processing of films

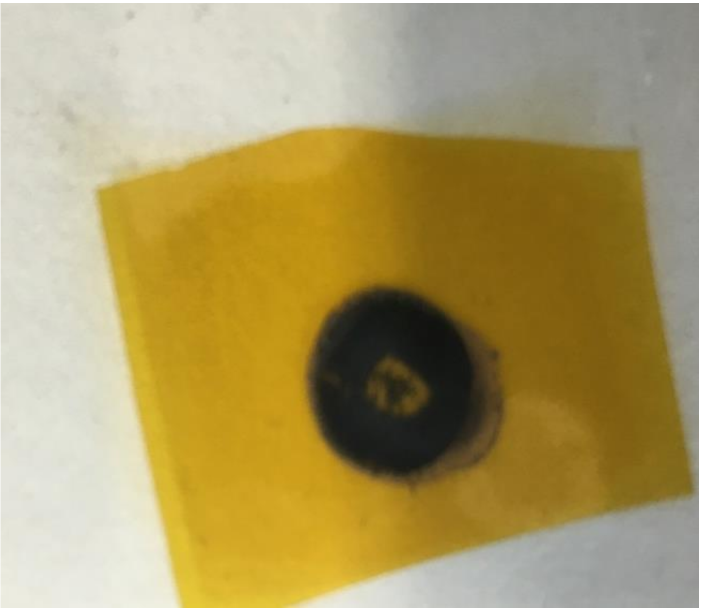
How about films during manufacture?



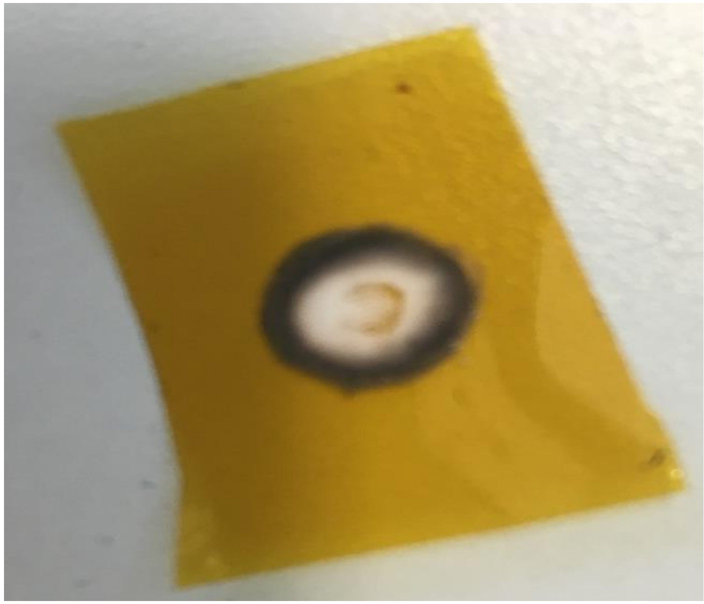
Cross section of PZT following heat treatment at 800°C for 4 hours

Bi_2Te_3 thick films – reaction with oxygen

10 min at 100°C in air

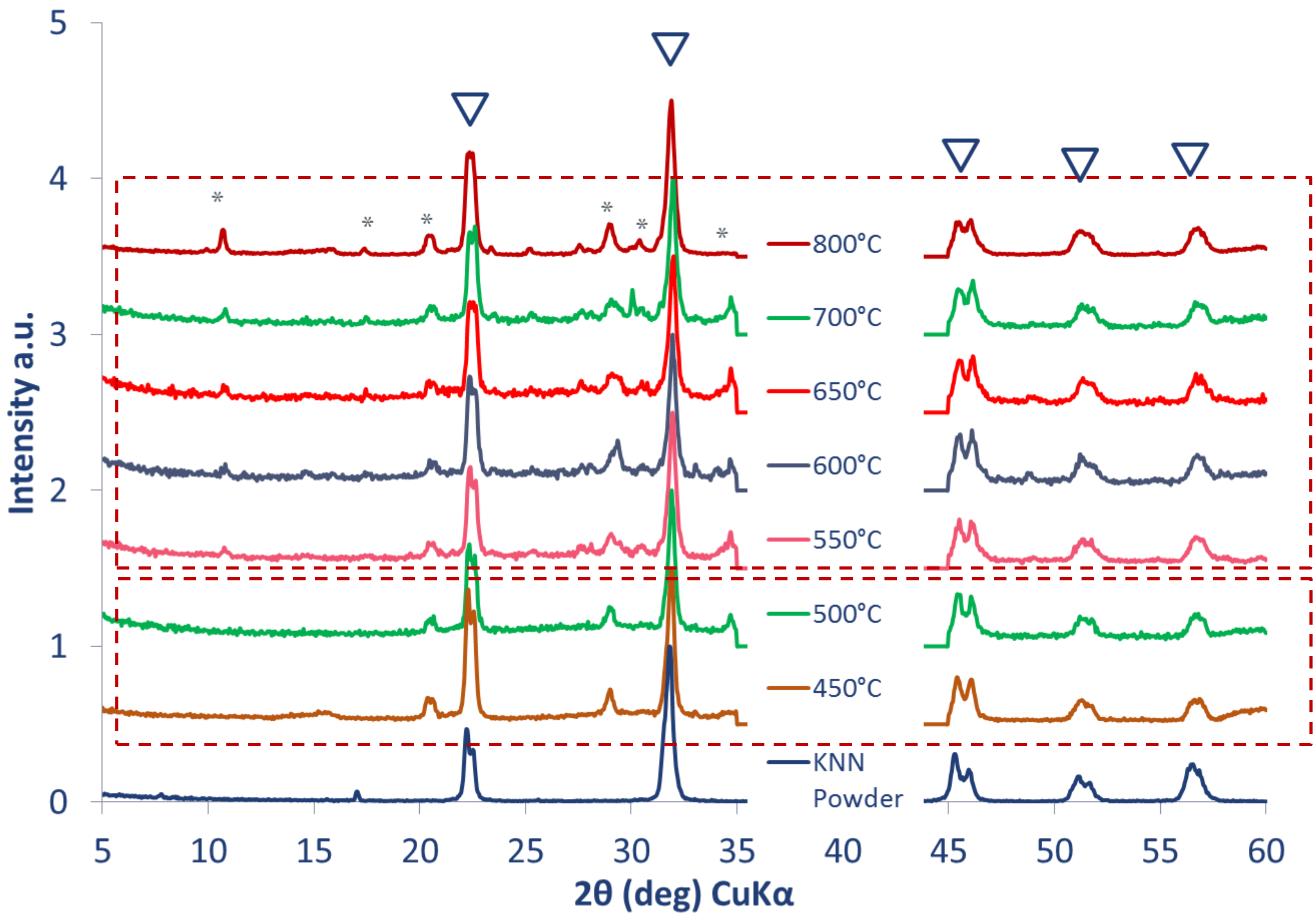


10 min at 350°C in air



Extensive reaction with atmosphere oxygen at low temperatures

KNN thick films - challenges

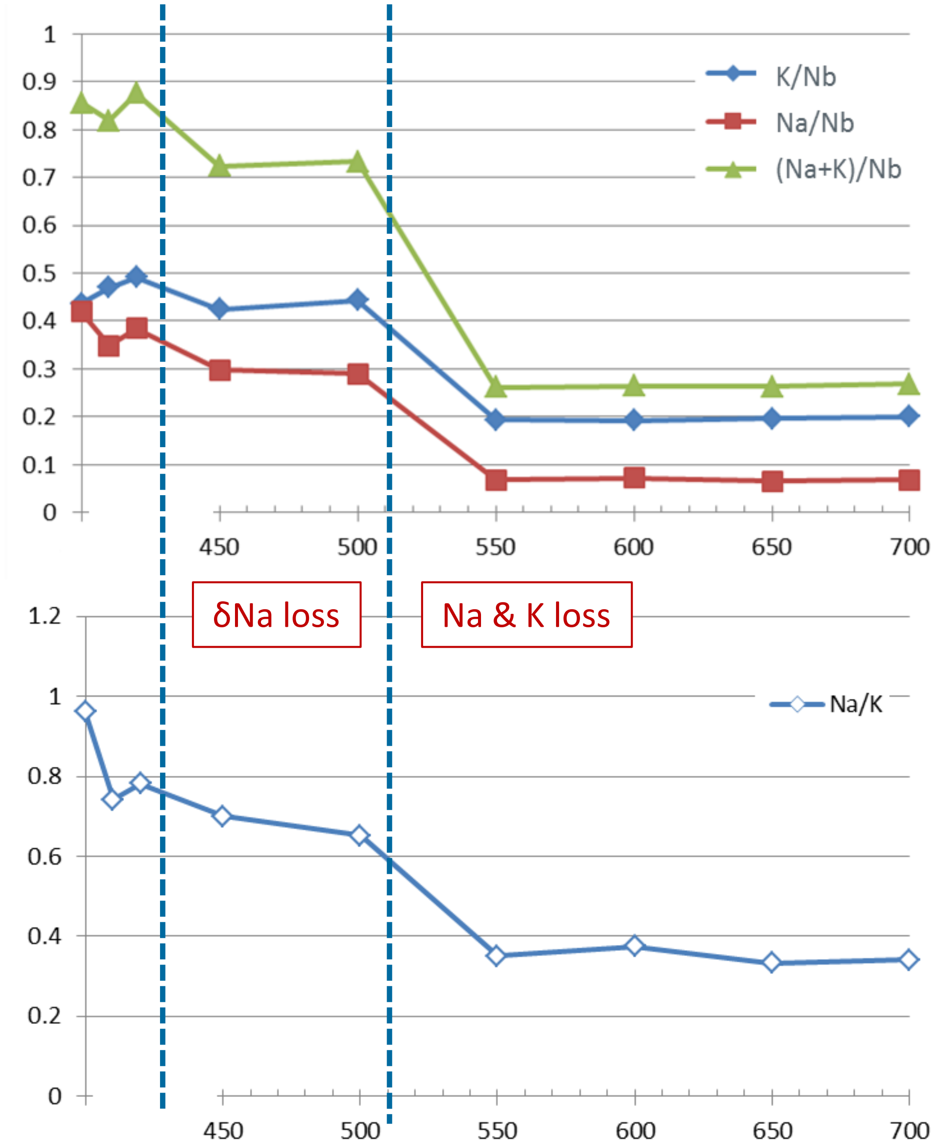


KNN thick films – loss of volatile elements

$K_{0.5}Na_{0.5}NbO_3$

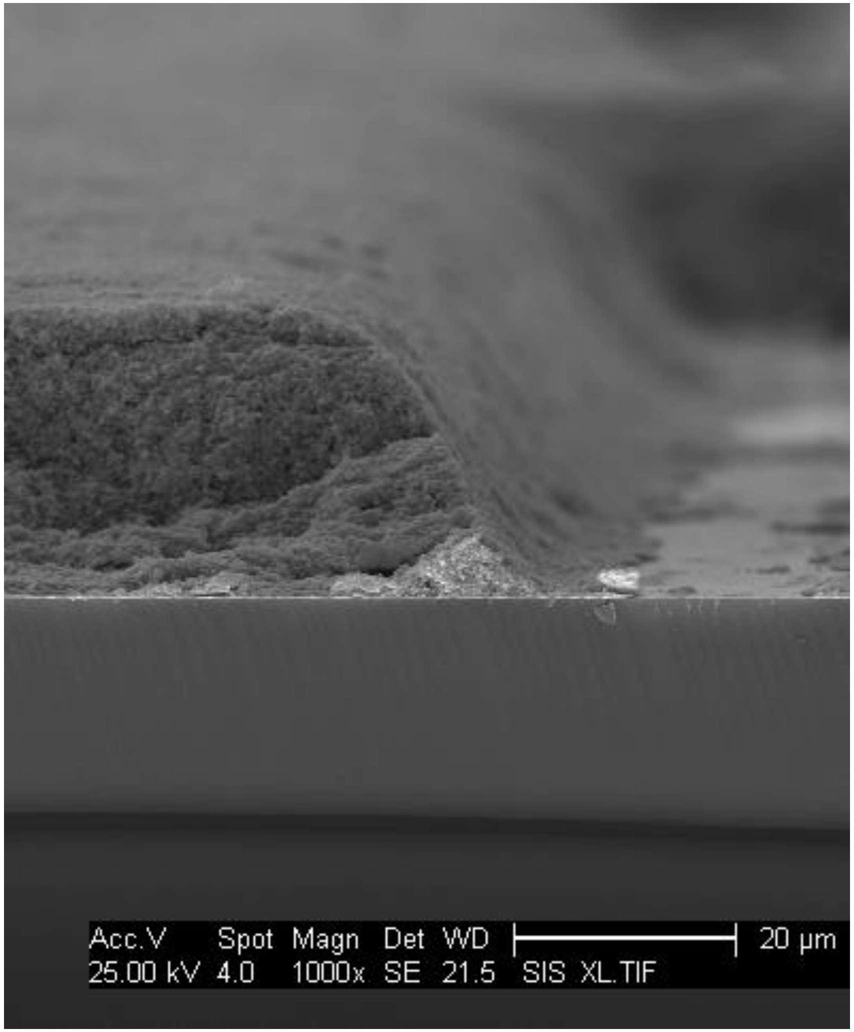
	Na At%	K At%	Nb At%
KNN Powder	22.6	23.5	53.9
Dried KNN sol	19.17	25.83	55
After deposition*	20.5	26.2	53.3
450°C/30 min	17.3	24.7	58.1
500°C/30 min	16.7	25.6	57.7
550°C/30 min	5.4	15.4	79.3
600°C/30 min	5.7	15.2	79.1
650°C/30 min	5.2	15.6	79.2
700°C/30 min	5.4	15.8	78.8

**200°C/1 min & 450°C/30 sec*



How about films during manufacture?

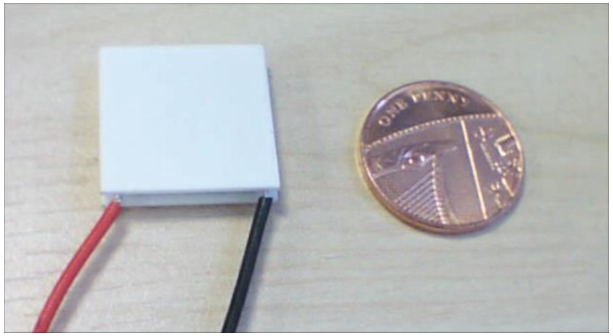
- Compositional fluctuations occur through-thickness of sample
- During early stages of sintering porous nature dominates for oxidation/evaporation effects
- Substrate interactions more important at longer times
- Substrate interactions lead to compositional gradient *(inward & outward diffusion)*
- Pattern has little effect provided aspect ratio > 1

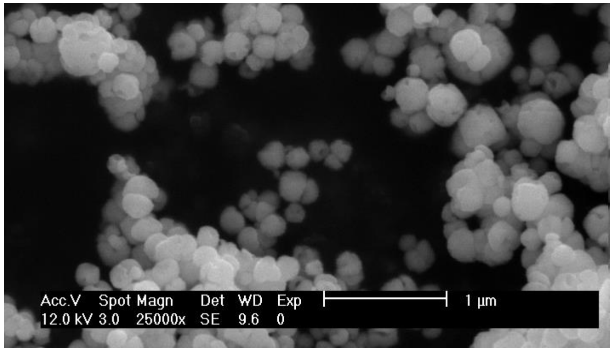


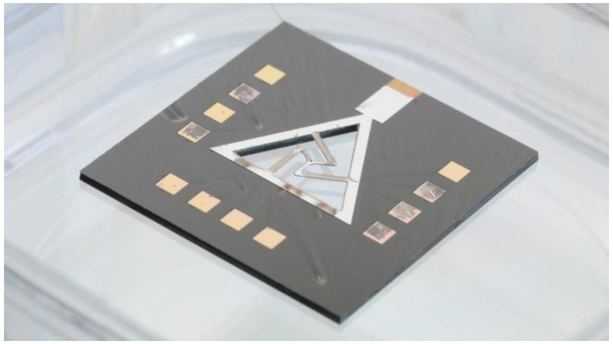
Summary

- Film forming techniques are continually improving
- Cheaper & quicker to fabricate than bulk systems
- Thick films are reliant on consolidation of powders
  i.e. heat required
- Control of content of volatile elements difficult to manage at T > 900°C without containment & excess.

Robert A. Dorey,
Integrated Powder-based Thick Films for Thermoelectric, Pyroelectric and Piezoelectric Energy Harvesting Devices
IEEE Sensors Journal, vol 14, no 7, pp 2177-2184, 2014







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