Reactive cold sintering

Dr Rebecca Boston

Lloyd's Register Foundation and Royal Academy of Engineering Research Fellow

University of Sheffield, UK

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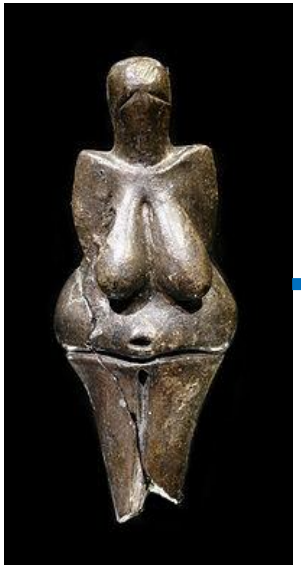
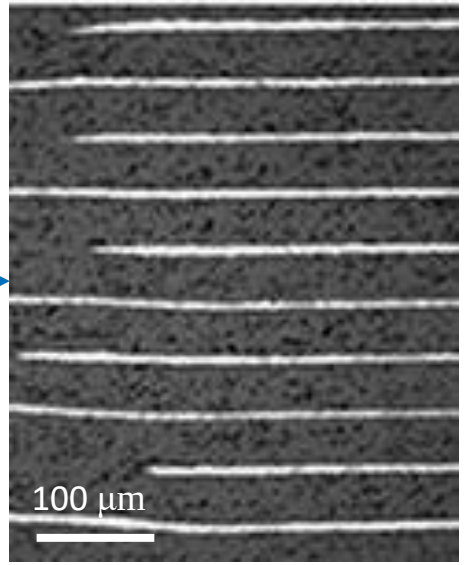
The long history of ceramics



Venus of Dolní Věstonice,
c. 25,000-29,000 BCE

Greek vase,
c. 680-420 BCE



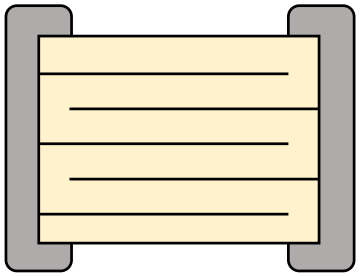
Multilayer ceramic
capacitor, 2017

Ceramics in modern technology

- Sintered ceramics are everywhere
- Often we lose properties due to
- the required sintering temperatures
- Energy intensive/expensive

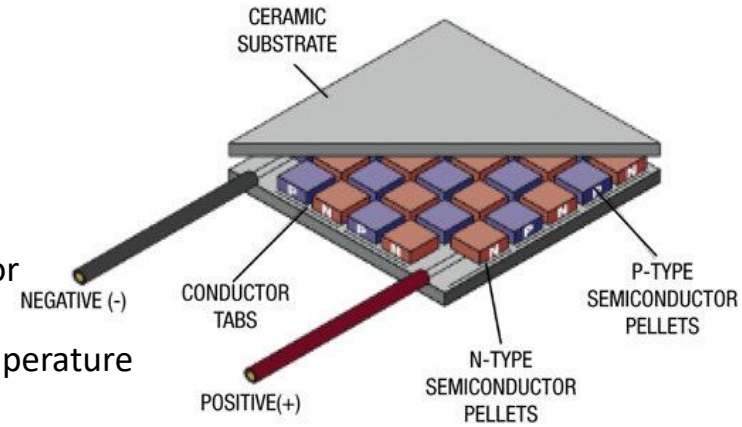
Sintered $Pb(Zr,Ti)O_3$ in headphones, accelerometers >1250 °C

Frit- car windscreens would never break except the frit has to be sintered on which reduces strength

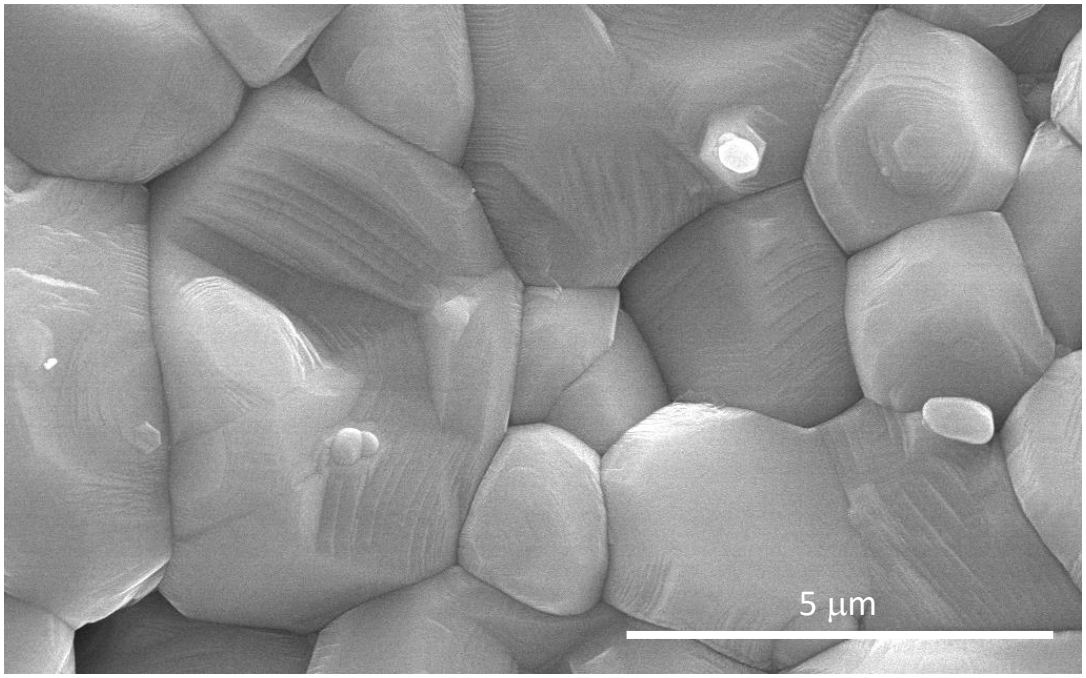


Multilayer ceramic capacitor
Doped $BaTiO_3$, Ni electrodes
Sinter at 1300 °C in argon

Thermoelectric generator
Two ceramics
Must sinter at same temperature



The sintering process



Grind

↓

Press

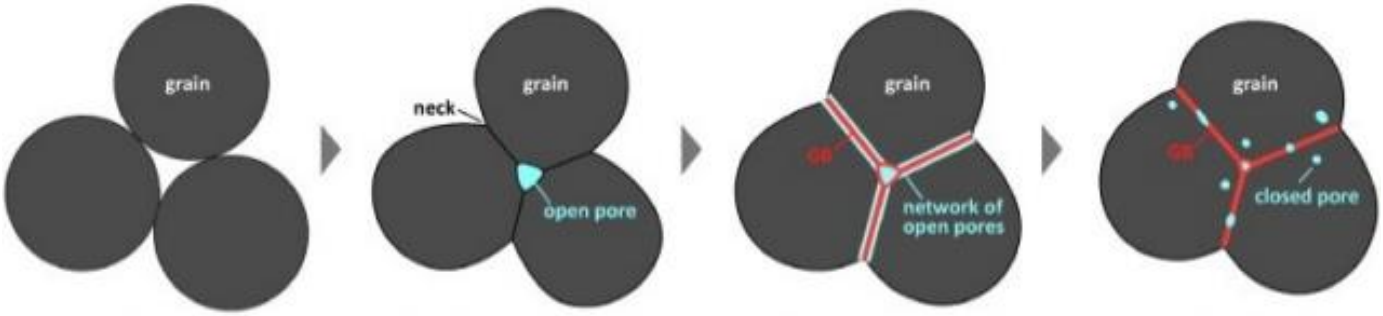
Uniaxial

CIP etc

↓

Heat

> 1200 °C



Current limitations

- High energy cost
- Slow
- Incompatible with polymers/electrodes
- Uncontrolled grain growth

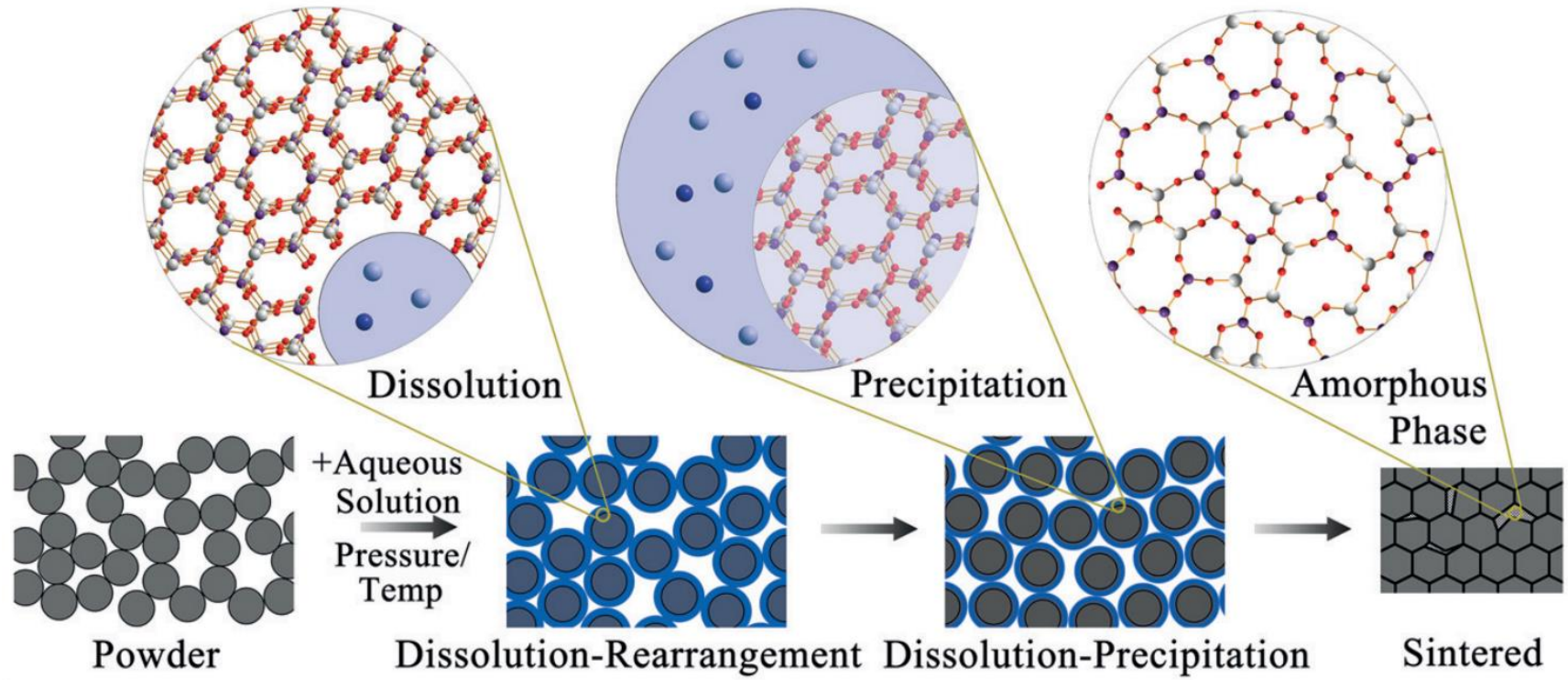
High temperatures required to achieve densification

Slow ramp rates (avoids cracking) and long hold times

High temperatures exclude many materials

No opportunity to retain/optimise nanostructure

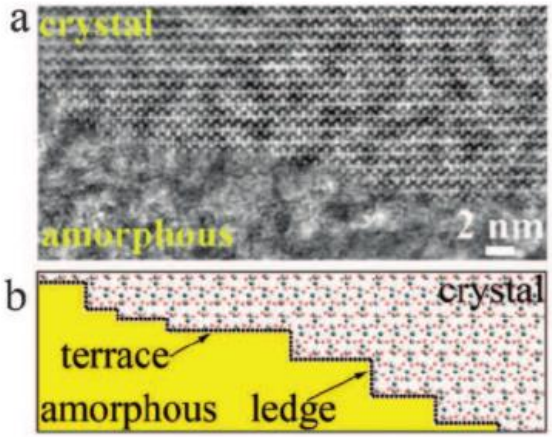
Cold sintering

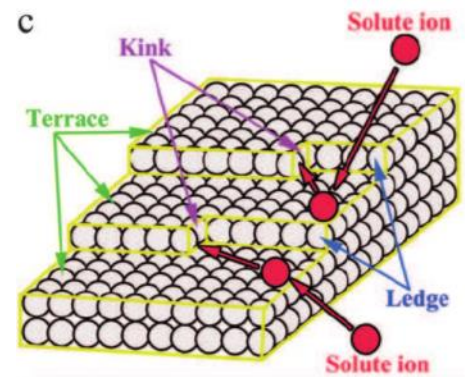


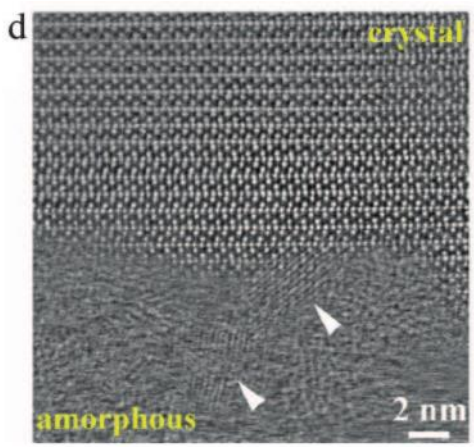
J. Guo et al, Angew. Chem., 55 (2016) 11457

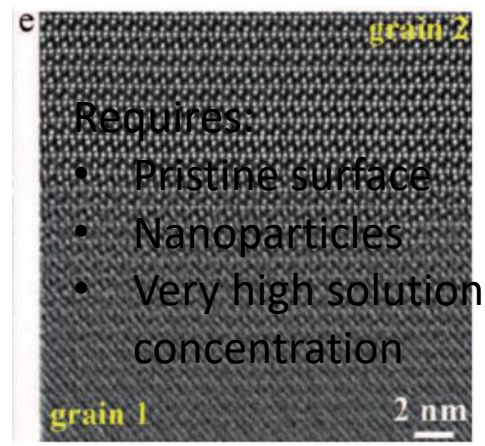
Cold sintering

Terrace-ledge-kink mechanism







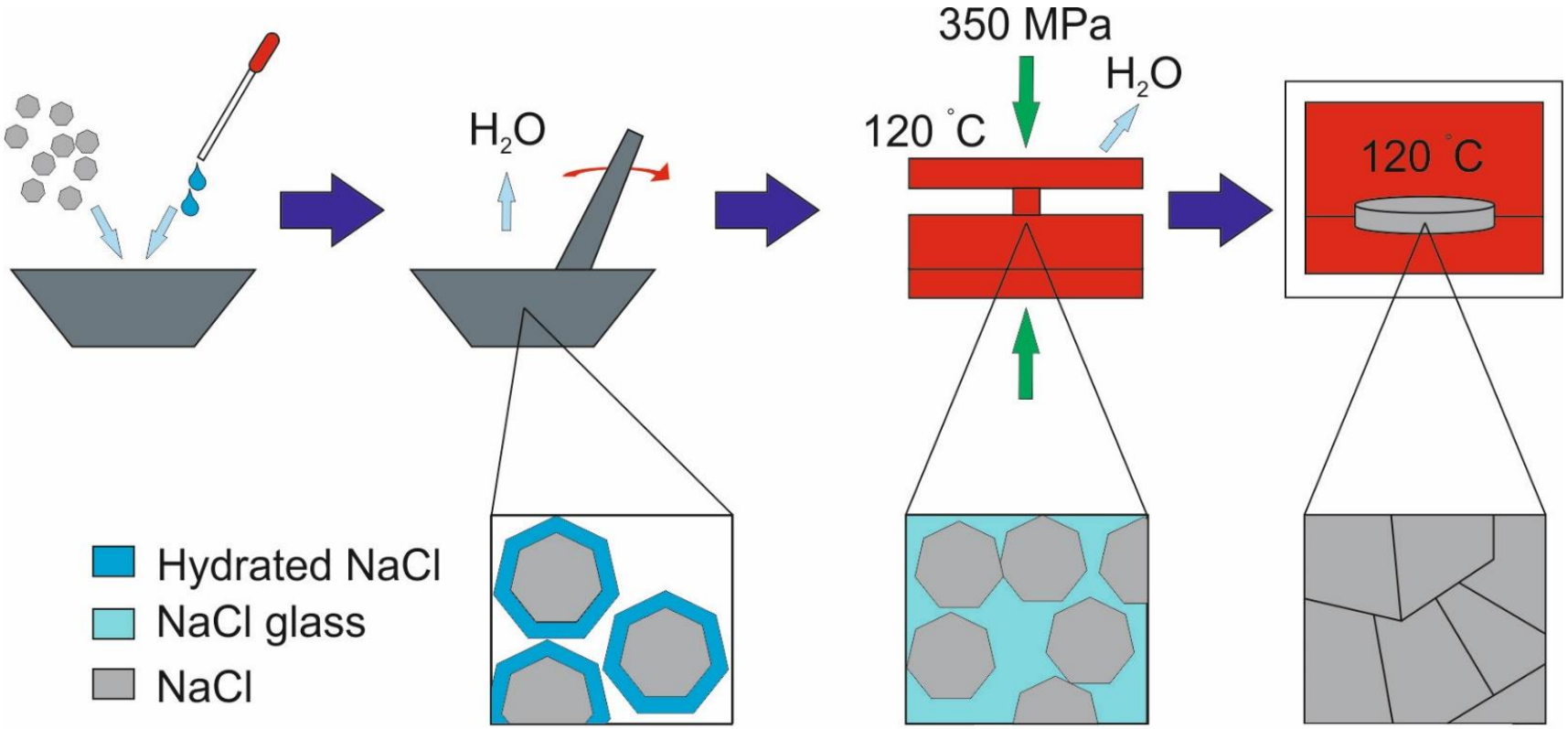


Requires:

- Pristine surface
- Nanoparticles
- Very high solution concentration

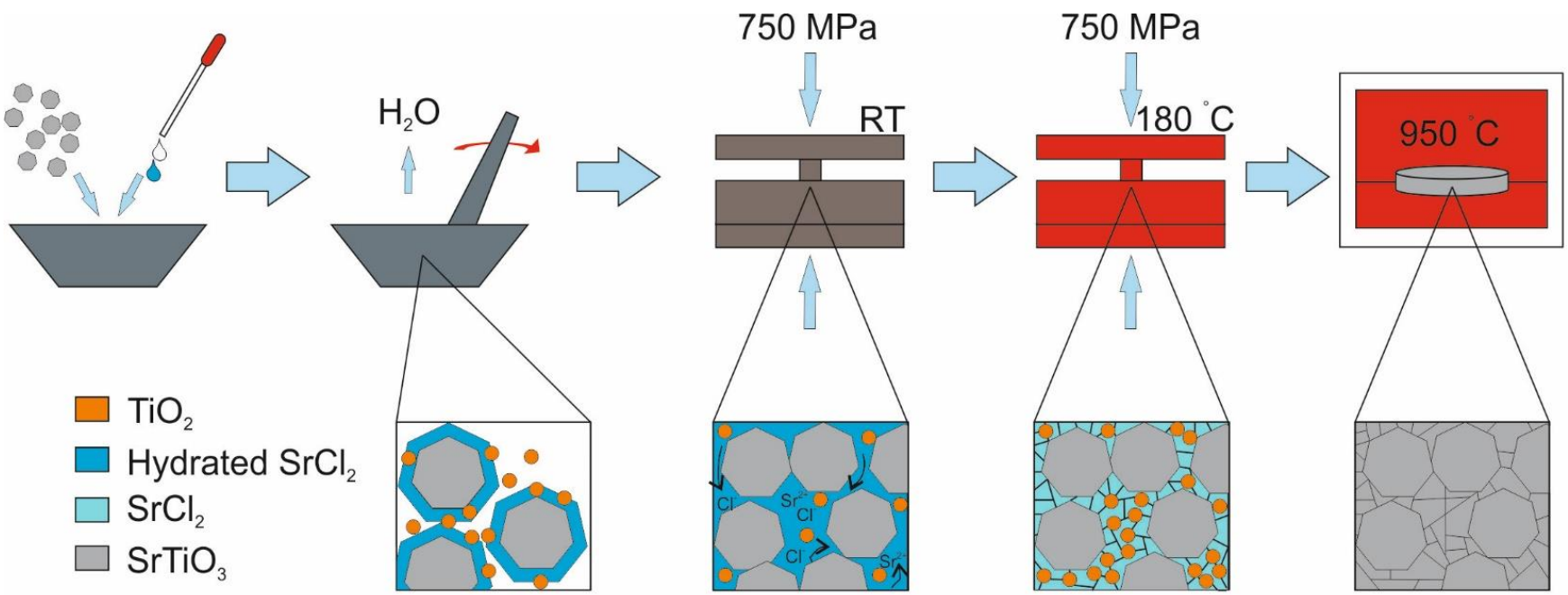
J. Guo et al, Angew. Chem., 55 (2016) 11457

Cold sintering: concepts



What happens if your material is not soluble?

Reactive cold sintering

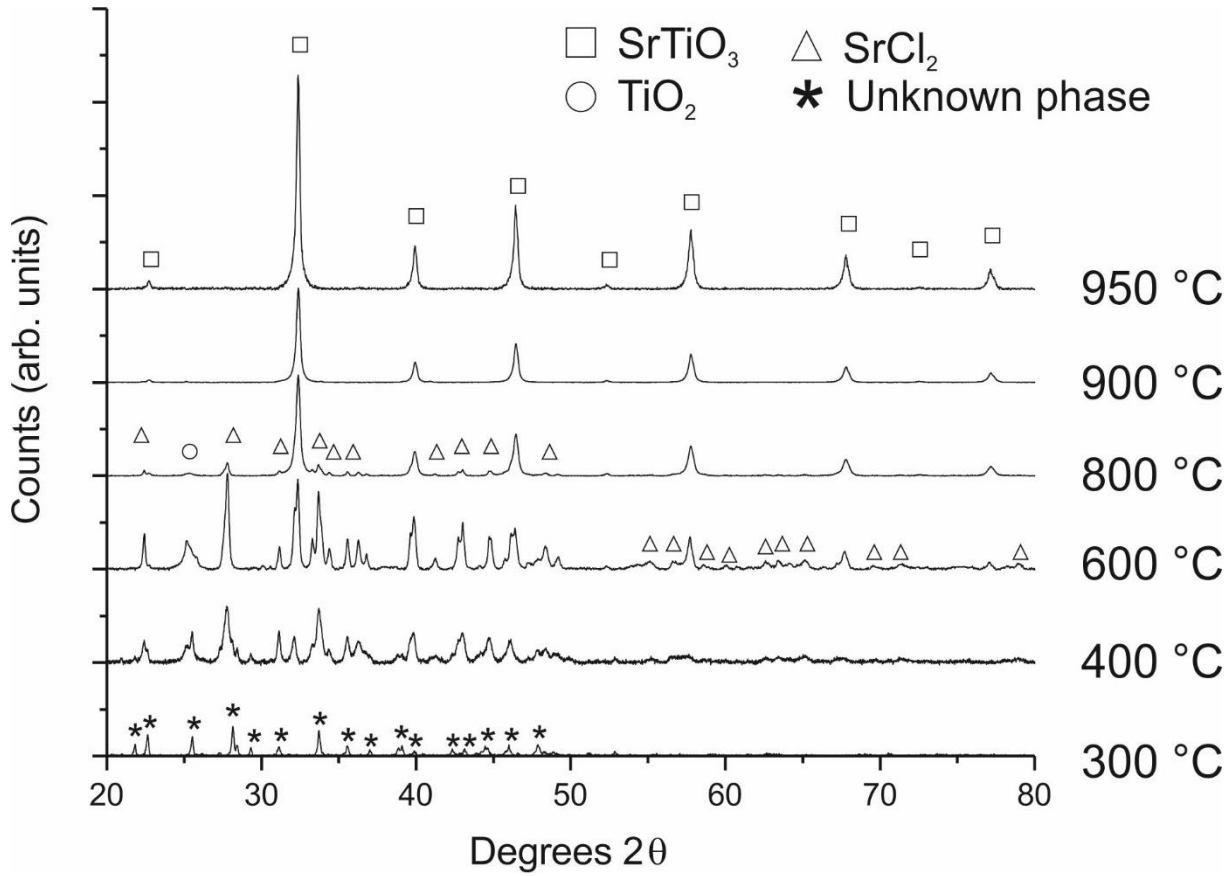


Any strontium titanate powder?

R. Boston et al, *RSC Adv. 2018*

Nanoscale $SrTiO_3$ synthesis

- $SrCl_2$
- TiO_2
- Water
- Forms nanoscale product

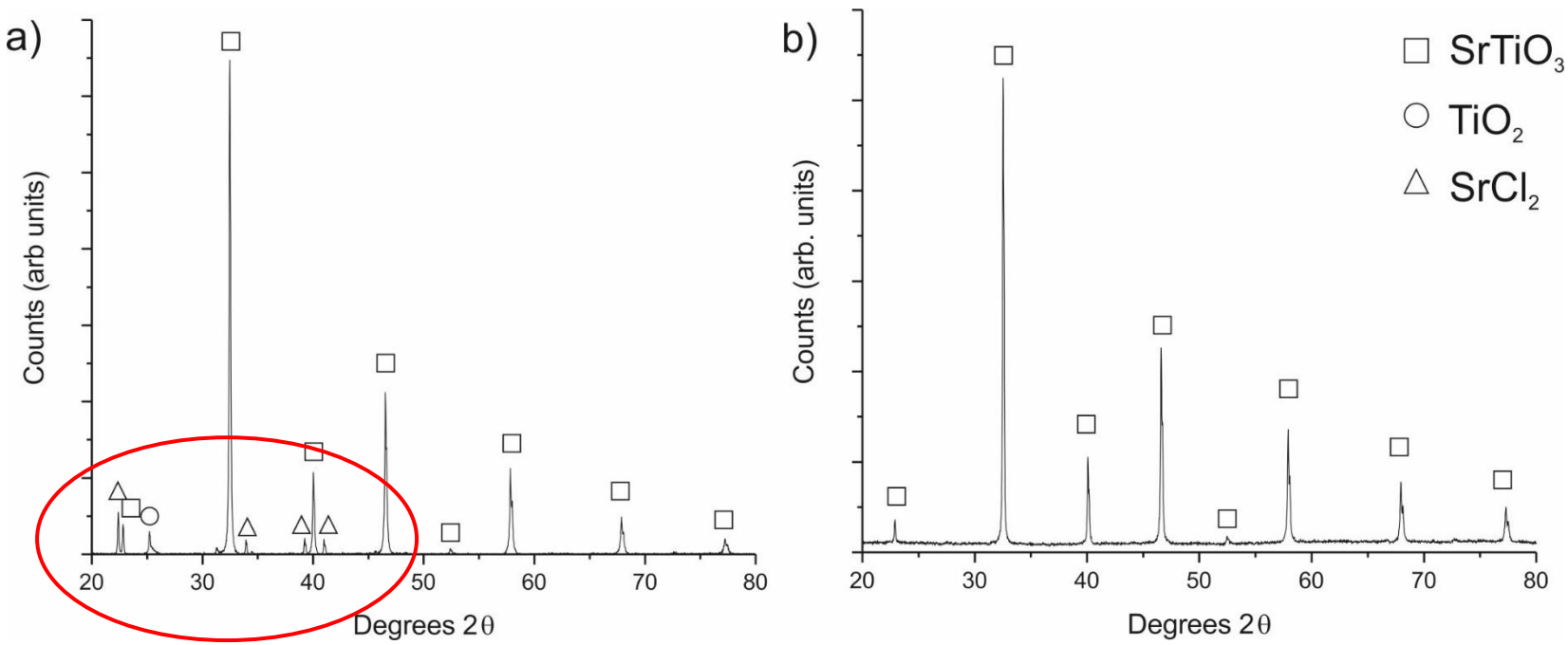


R. Boston et al, *Inorg. Chem.* 2017,
R Boston et al. *RSC Adv. 2018*

Intermediate phase interactions

Post cold-sinter (180 °C)

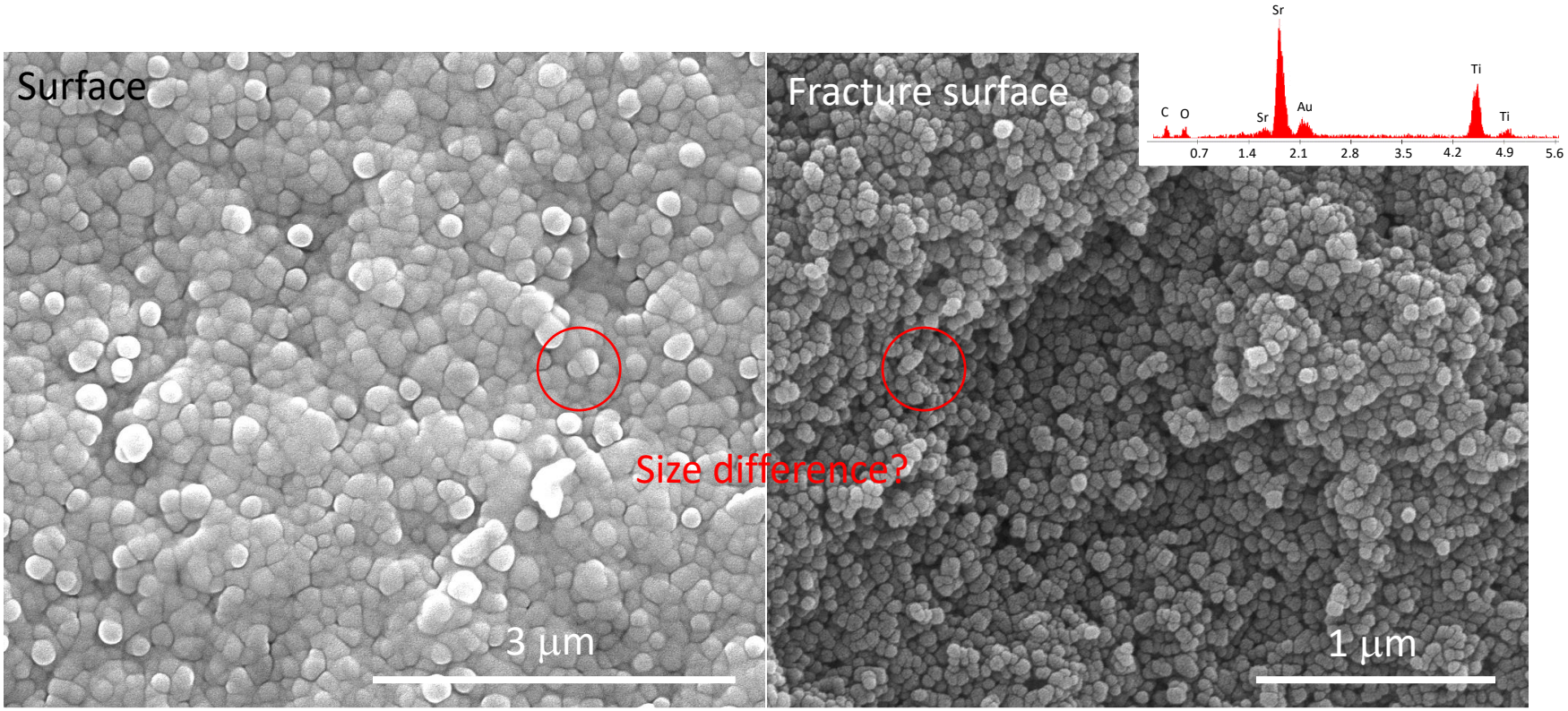
Post anneal (950 °C)



R. Boston et al, *in preparation*

Strontium titanate- nanoscale

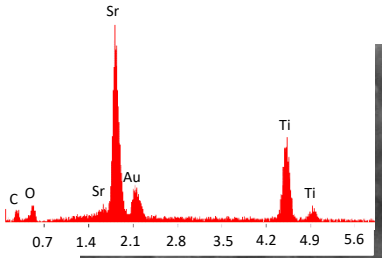
>97 % dense at 950 °C (1400 °C is normal sintering temperature)

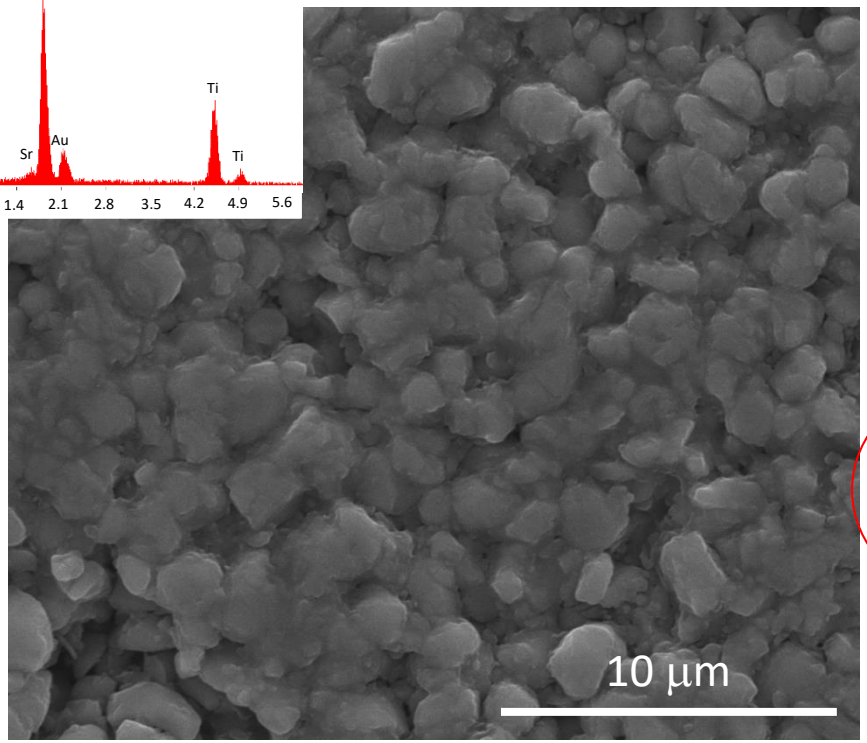


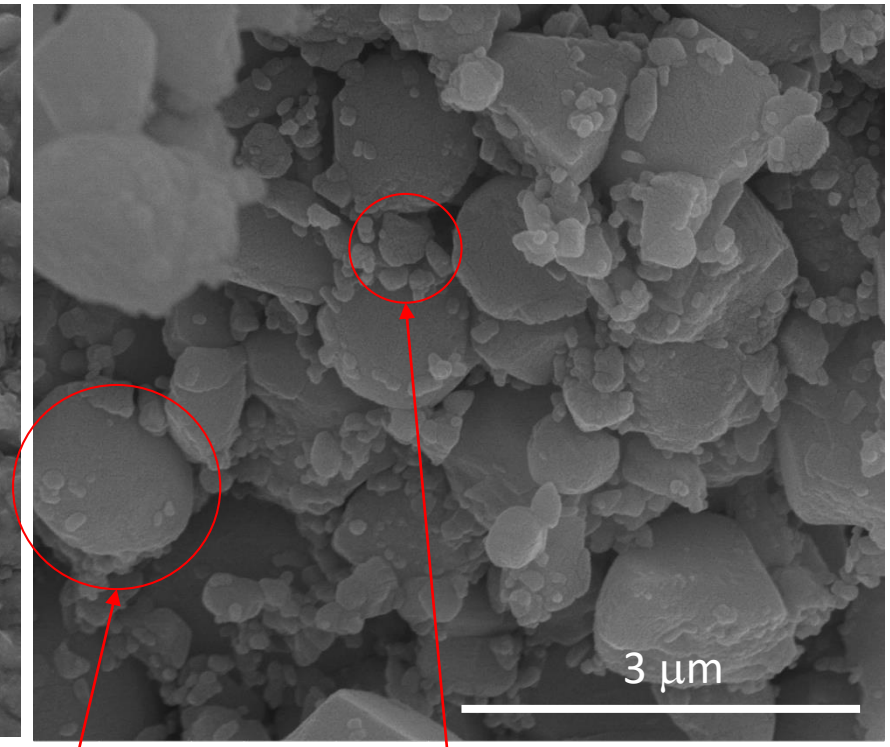
R. Boston et al, *RSC Adv. 2018*

Strontium titanate- micron scale

>96 % dense at 950 °C (1400 °C is normal sintering temperature)





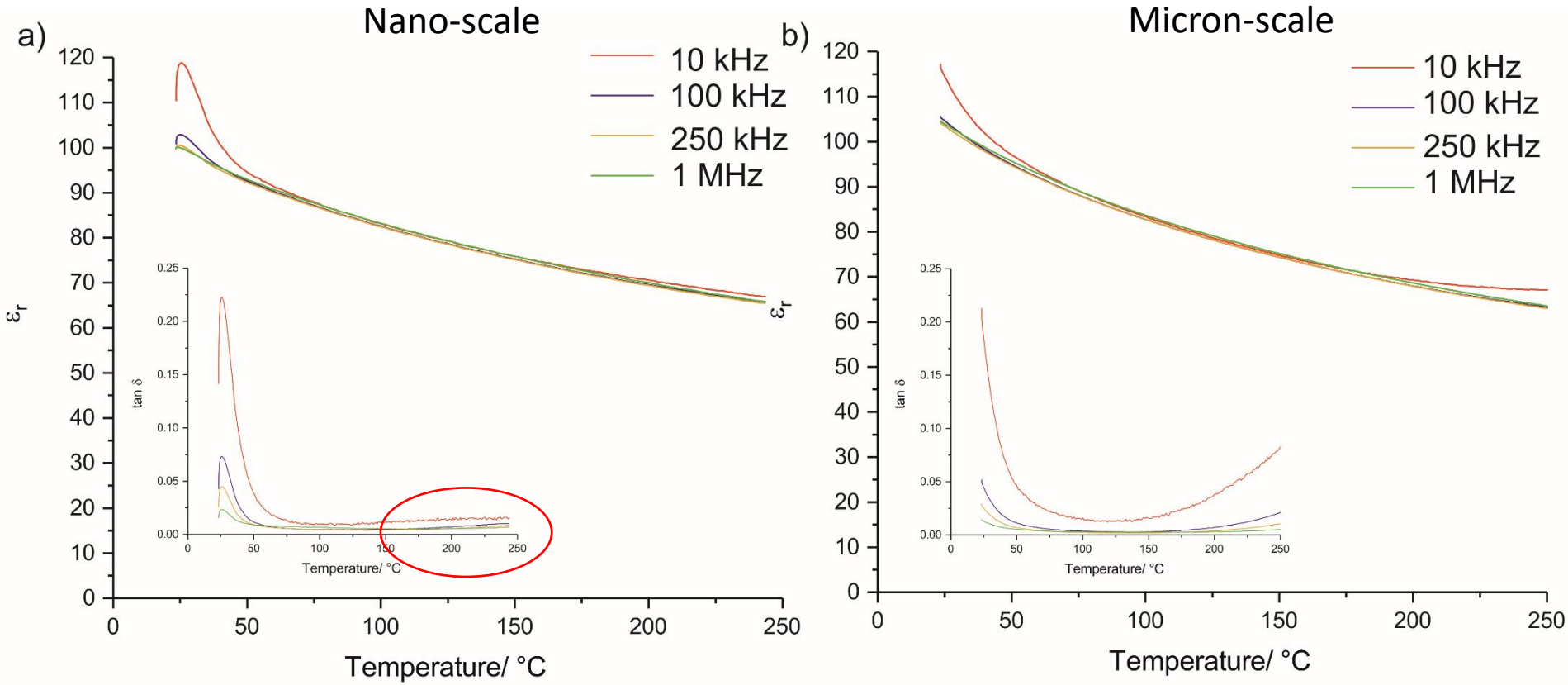


Starting powder

Infill phase

R. Boston et al, *RSC Adv. 2018*

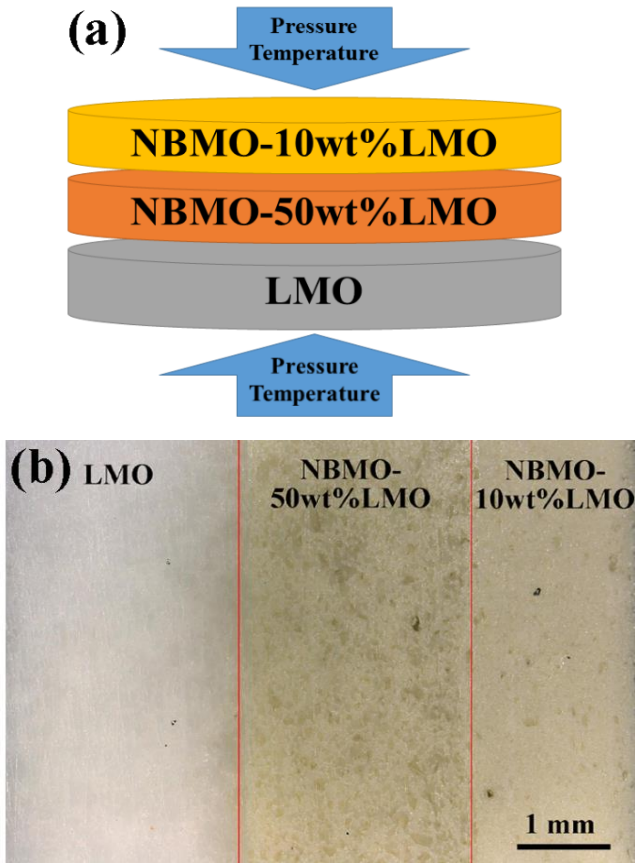
Permittivity



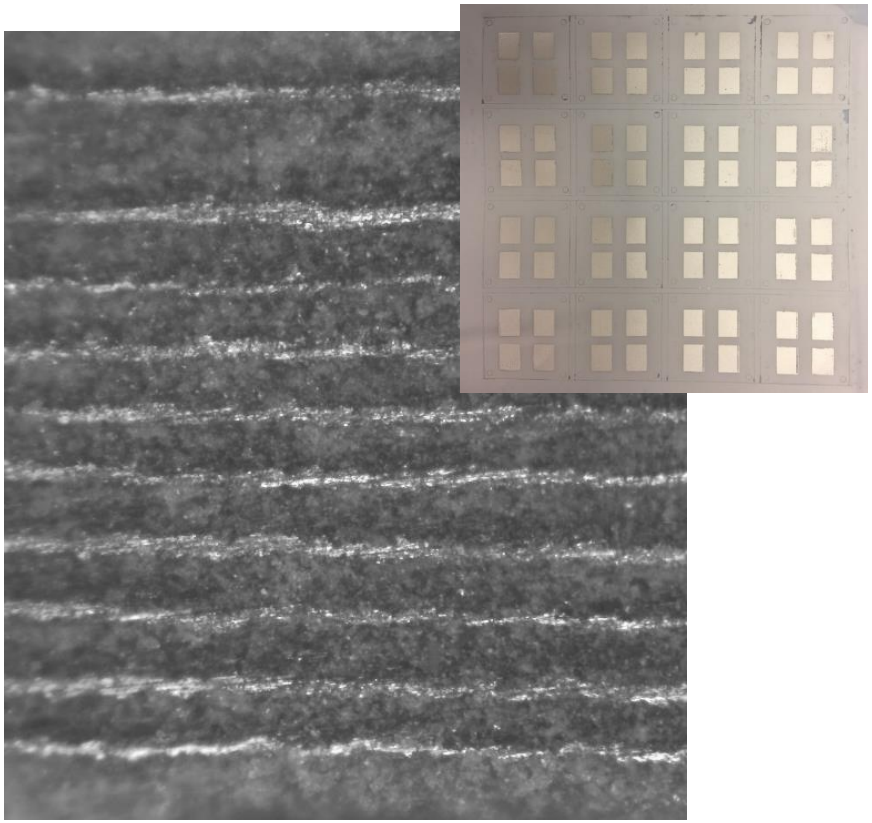
Lower high-temperature losses

R. Boston et al, *RSC Adv. 2018*

Cold sintering: the future



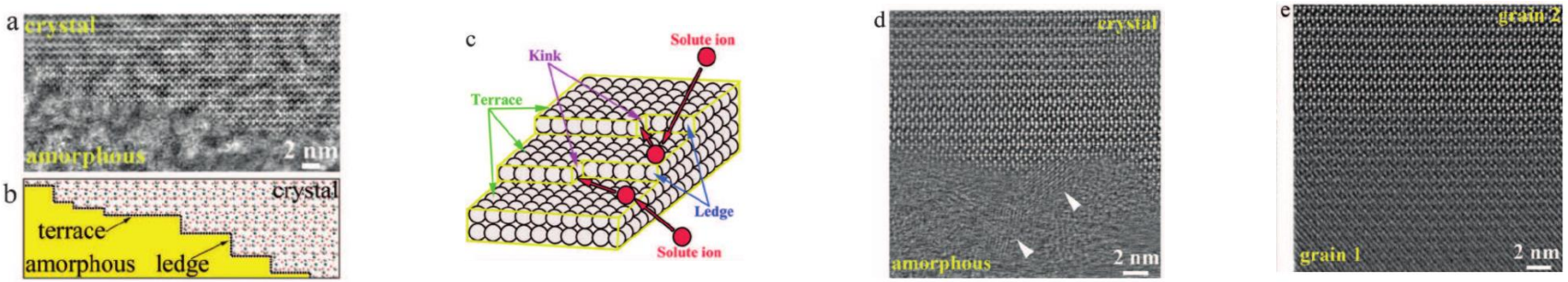
D Wang et al, submitted Adv. Func. Mater., 2017



I M Reaney et al, after Randall et al, 2016-17

Summary

- Cold sintering now demonstrated for a wide range of materials
- Potential to unlock new composite materials
  - Ceramic-ceramic
  - Ceramic-polymer
  - Ceramic-metal
- Original cold sintering limited to soluble materials
- Reactive intermediate phase cold sintering has wider applications
  - Any size or quality of powder
  - Easy creation of ceramic-ceramic composites
- Route to sustainable sintering of ceramics
- Still exploring the applications and possibilities



Acknowledgements

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Funders

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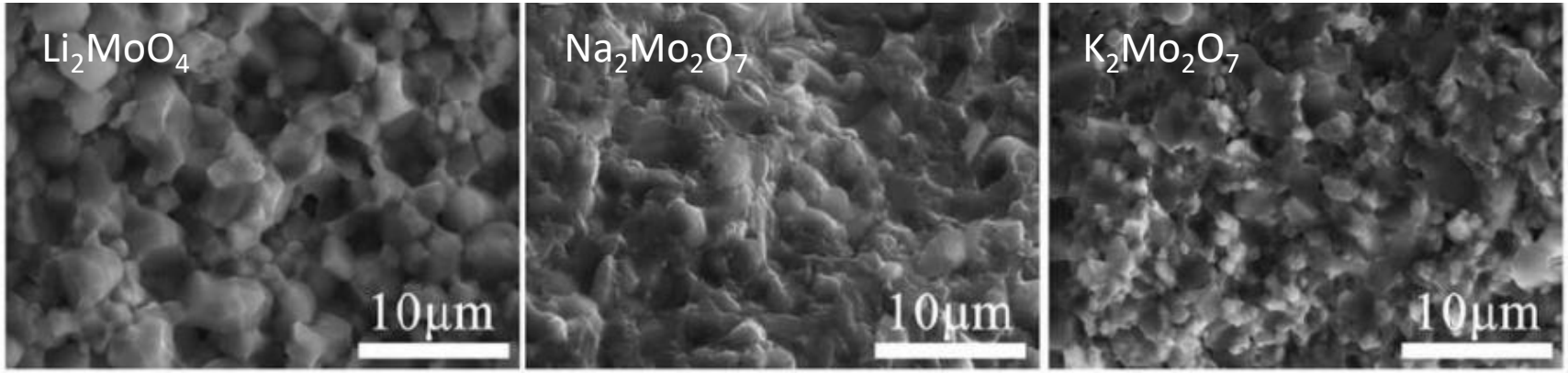
- Royal Academy of Engineering
- EPSRC

Initial discoveries



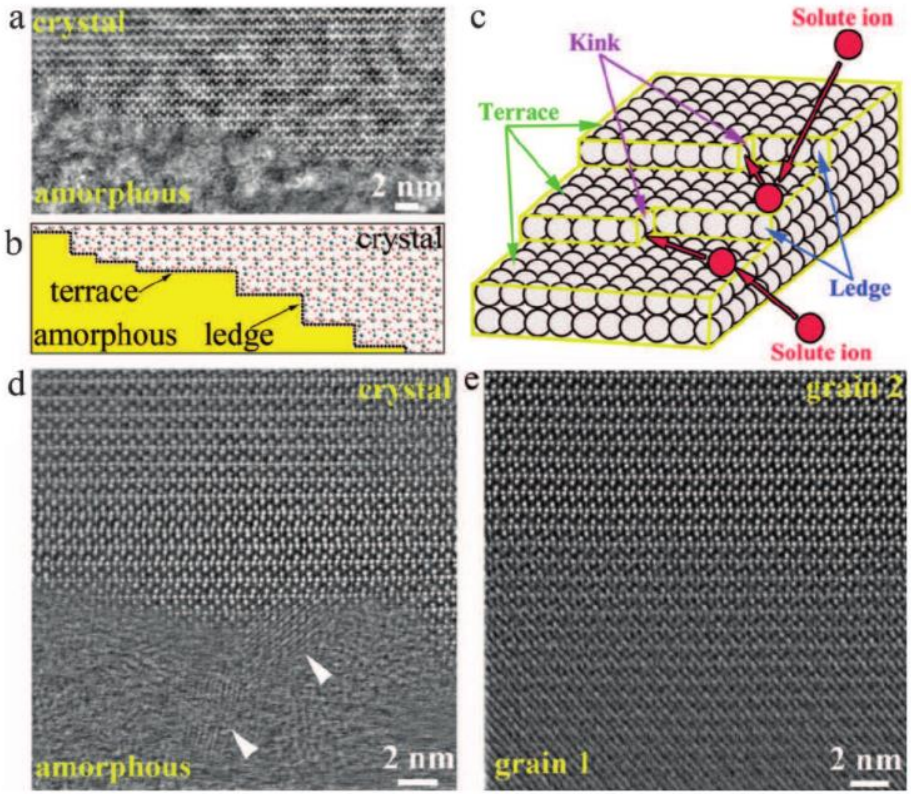
Li_2MoO_4	$Na_2Mo_2O_7$	$K_2Mo_2O_7$
ρ 95.5 %	ρ 93 %	ρ 94.1 %
ε_r 5.61 (5.5)	ε_r 13.4 (12.9)	ε_r 9.8 (7.5)

120 °C and 350 MPa for 15 min followed by 6h at 120 °C anneal

J. Guo et al, Angew. Chem., 55 (2016) 11457

Mechanism

- Terrace ledge kink model for crystal growth
- Amorphous phase attributed to rate of solute condensation
- Step edges thermodynamically favourable for surface diffusion



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Congruent vs incongruent materials

- Not all materials solubilise in the same way
- Sr can solubilise from lattice
- Forms Ti-rich glass
- Blocks TLK growth
- Prevents cold sintering