The reducing atmosphere of the Spark Plasma Sintering: a disadvantage or an advantage for oxides?

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Fabien GIOVANNELLI, E. Bsaibess, E. Sabarthes, D. Brault, M. Bah, R. Retoux, M. Pitcher, E. Veron, C. Genevois, M. Allix, M. Zaghrioui, F. Delorme, I. Monot-Laffez.

Summary

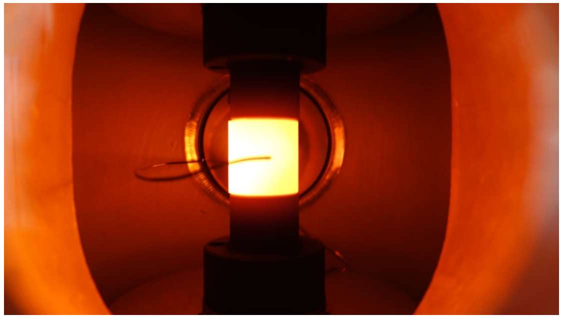
1- Piezoelectric material : $K_{0.5}Na_{0.5}NbO_3$ (KNN)

2- Thermoelectric oxide : $Sr_{0.95}La_{0.05}TiO_3$.

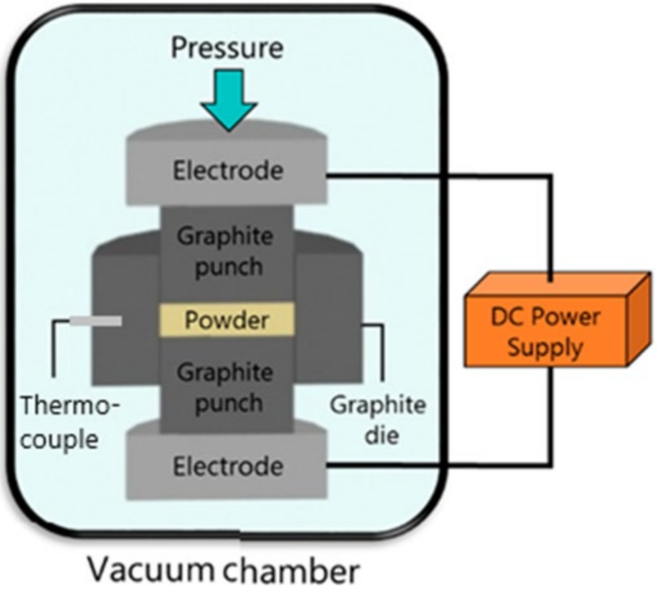
3- Thermoelectric oxide :$La_{0.66}Ti_{0,95}Al_{0.05}O_3$

4- Ionic conductor: $La_2Mo_2O_9$

Spark plasma sintering – a way for high relative densities



SPS 632Lx –Fuji Electronics
3000 A – 60 kN



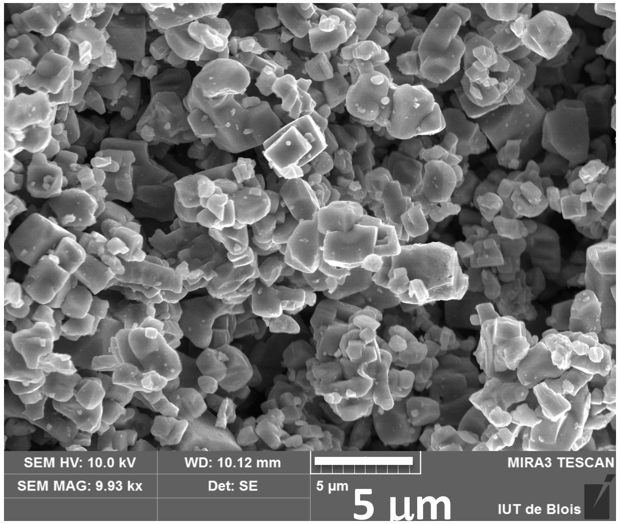
<u>Benefits:</u>
- Lower temperature – shorter time
- Prevent alkali volatilization
- High relative densities

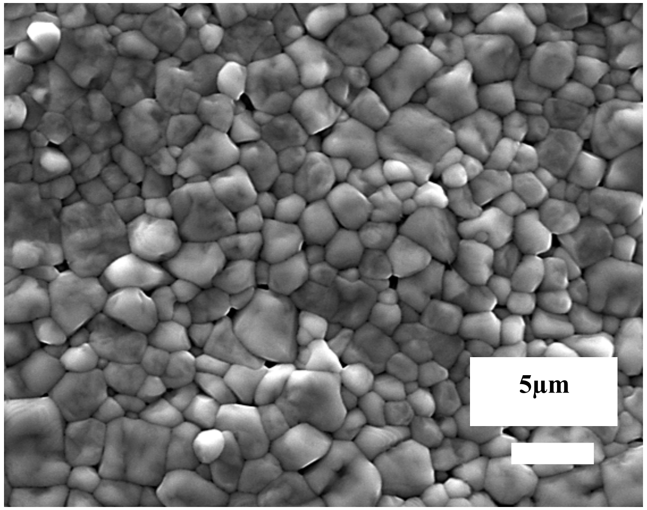
<u>Drawbacks ?</u>
- C contamination with graphite materials ?
- Reductive conditions / oxygen losses ?
- Densification mechanisms: creep/ defects ?

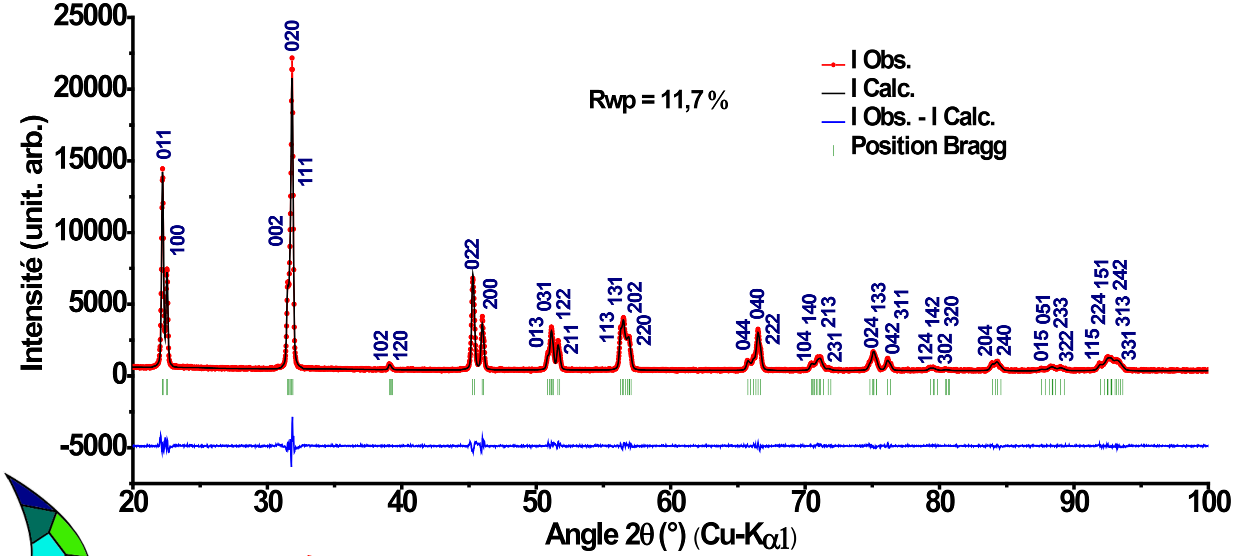
Impact of SPS on piezoelectric material : $K_{0.5}Na_{0.5}NbO_3$ (KNN)

KNN, $K_{0.5}Na_{0.5}NbO_3$

SPS - 920°C - 98% - 3µm







Orthorhombic, *Amm*2

a = 3.945 Å

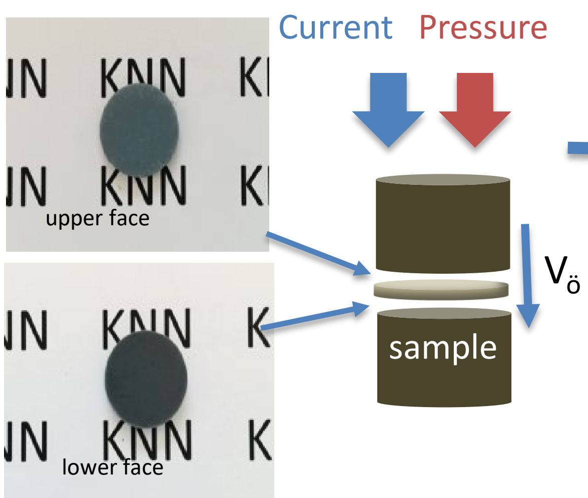
b = 5.646 Å

c = 5.678 Å

M. Bah et al. Ceramics International 40 (2014) 7473

What about drawbacks ?

25-50 MPa



> 1000 A

O_2

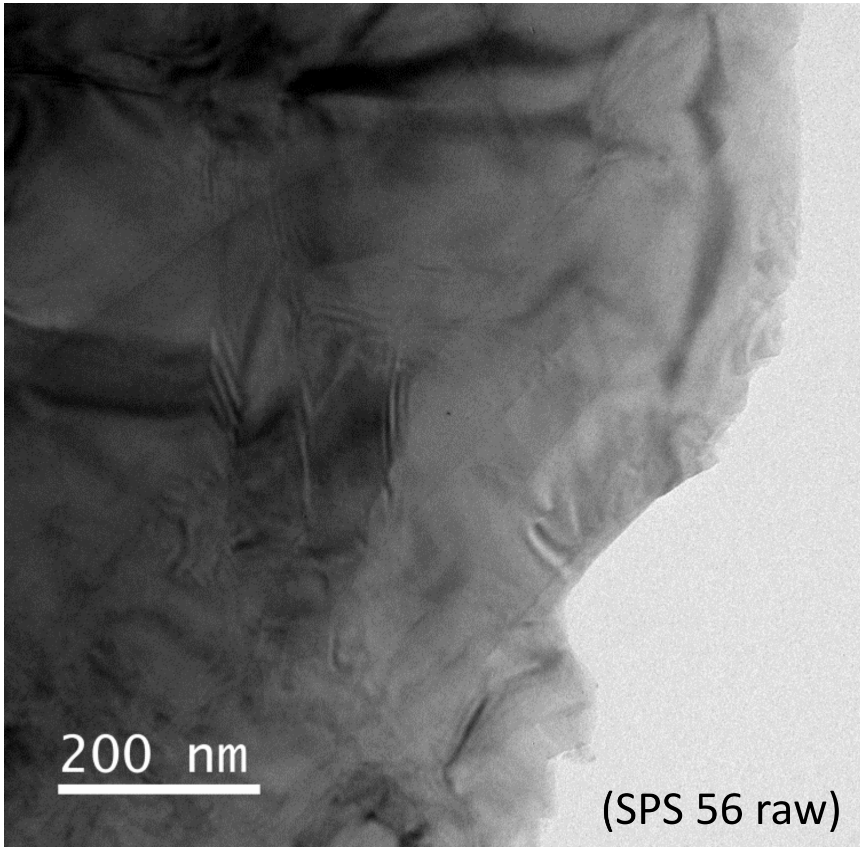
Raw material , post SPS
(dark grey or dark blue)

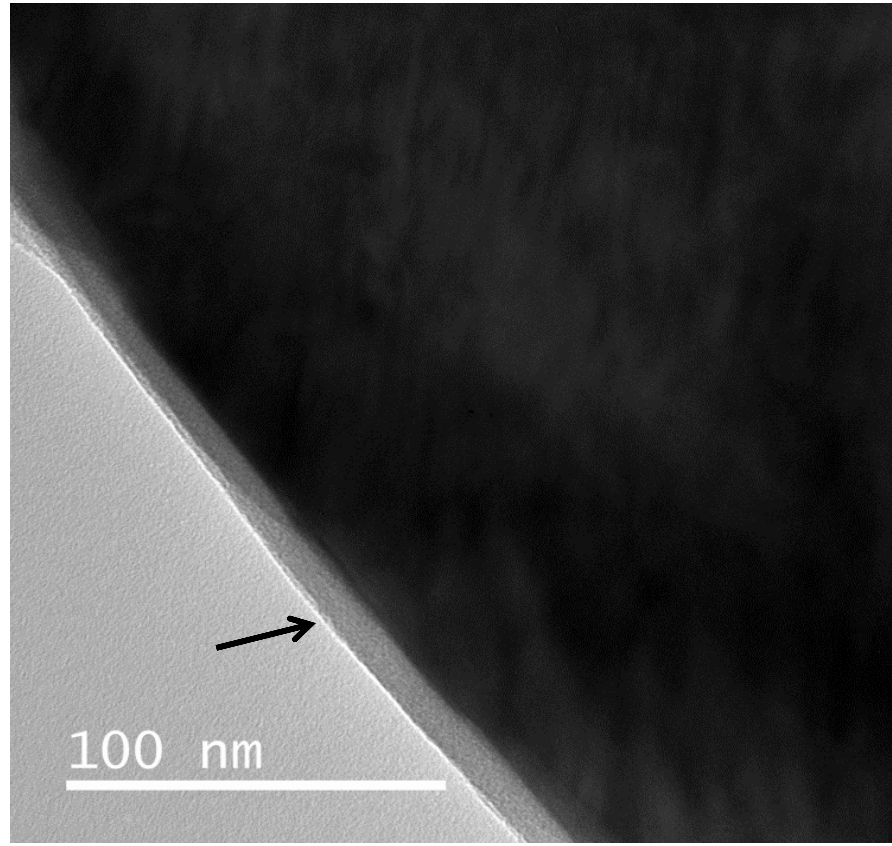
After oxygen annealing
600-900°C – 60°C/h
(milky-white)

Oxygen losses ?
C contamination ?

Better electromechanical properties

Defects in raw KNN SPS sintered





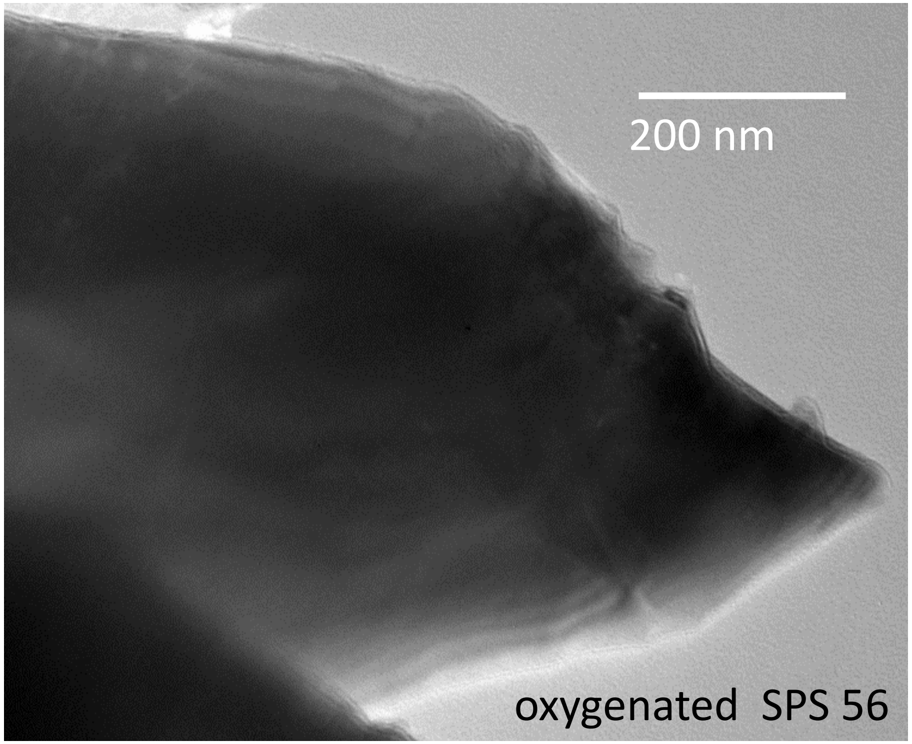
a

disturbed contrasts
→ stresses
→ crystallites' defects

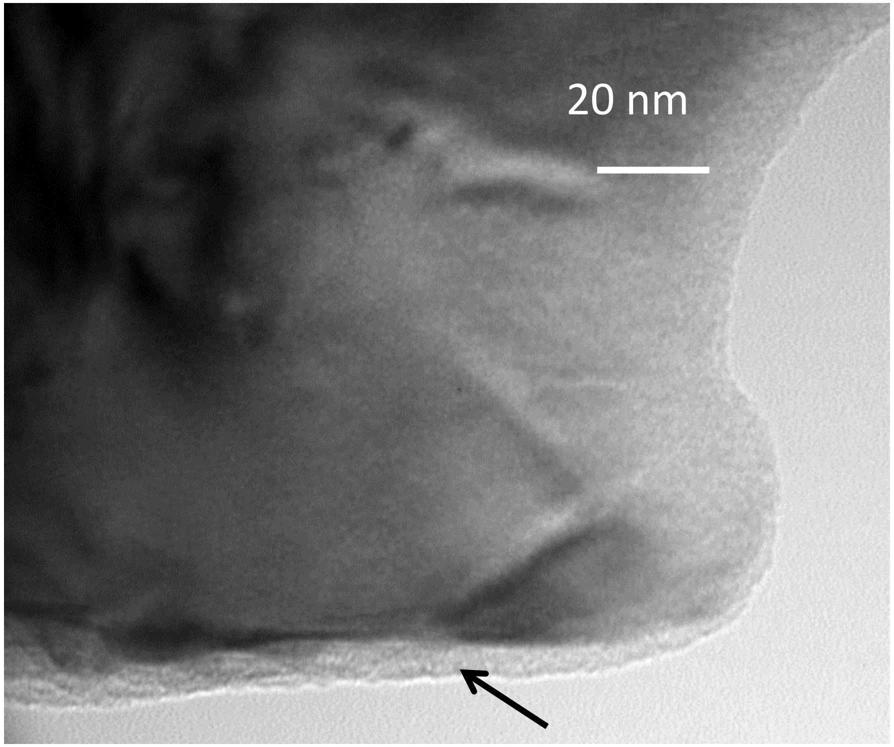
b

Systematically,
amorphous carbon strips (few nm) around the grains.

After oxygen annealing



a



b

Regular and homogeneous contrasts → low stress → Low defects.

No more C on grains' edge

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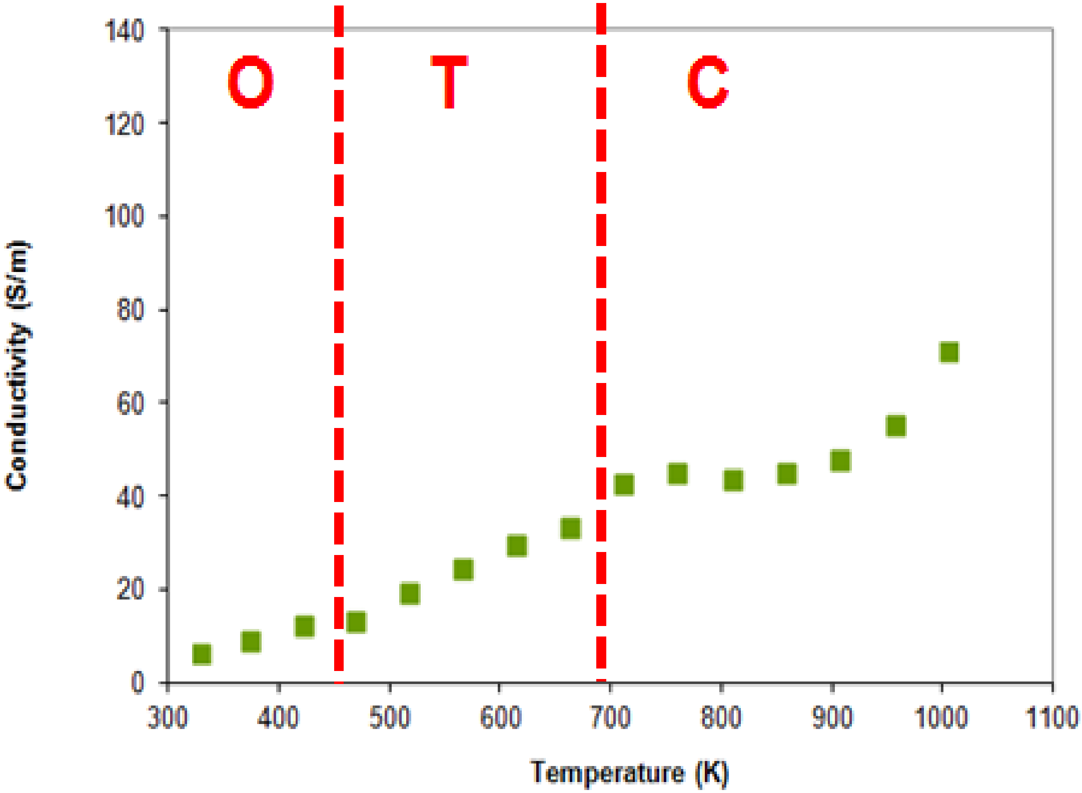
OXYGEN ANNEALING supresses C contamination, stresses and defects

Monot-Laffez et al. Eur. Phys. J. Spec. (2022) 231:4185

raw SPS-KNN : Electrical conduction

Charge carriers

Oxygen vacancies



Oxygen annealing

NO MORE conductivity

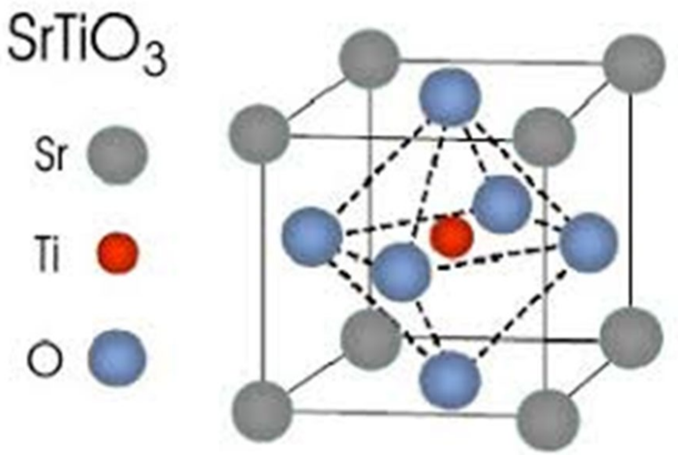
Easy to recover oxygen content

F. Delorme et al. Materials Letters, Vol. 162 (2016) 24

Impact of SPS on thermoelectric oxide : $Sr_{0.95}La_{0.05}TiO_3$

$$ZT = T\,S^2\sigma/\kappa = T\,PF/\kappa$$

S = Seebeck coefficient (µV/K)
σ = Electrical conductivity ($S.m^{-1}$)
κ = Thermal conductivity ($W.m^{-1}.K^{-1}$)
PF = Power factor ($W.K^{-2}.m^{-1}$)



- Perovskite structure

- N-type Semiconductor with a band gap of 3,2 eV

- La substitution = High Power factor : 2 10^{-3} W/m K^2

Okuda et al. Physical Review B 63 (2001) 113104.

- High thermal conductivity : 7 – 4 W/ m K

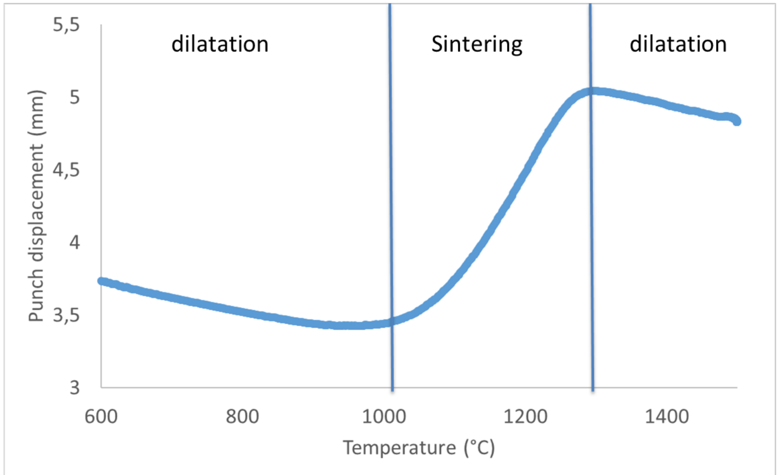
Muta et al. Journal of alloys and compounds 350 (2003) 292?

$$Sr_{0.95}La_{0.05}TiO_3$$

Optimized properties require sintering under Ar/H_2 or long term annealing at 1400°C under Ar/H_2 after sintering

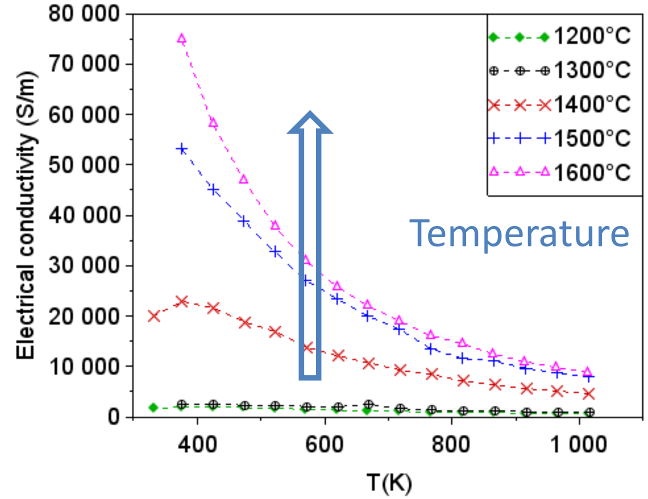
⇨ **SPS**

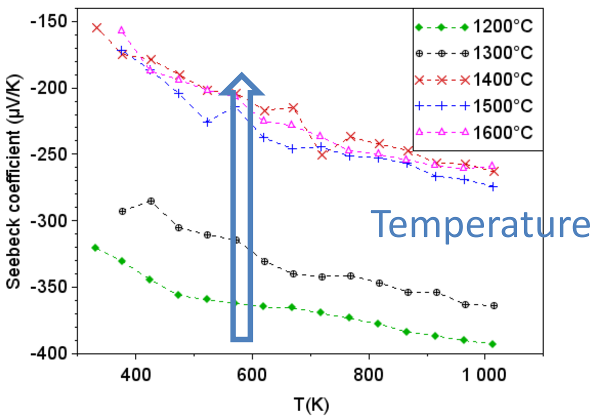
SPS Conditions

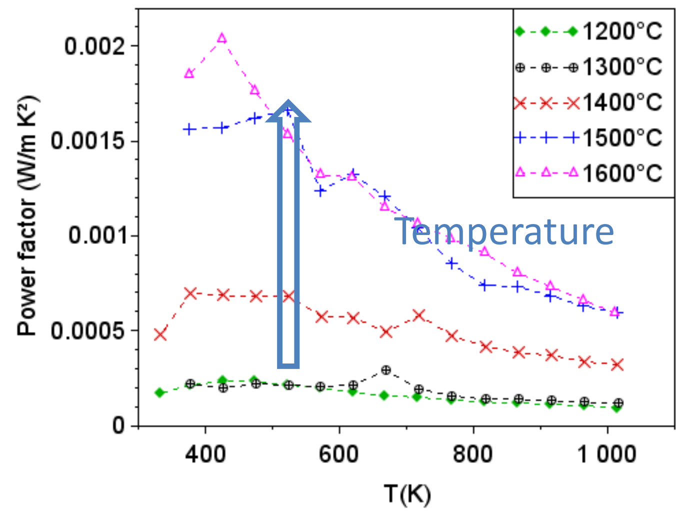


80 MPa

10 min

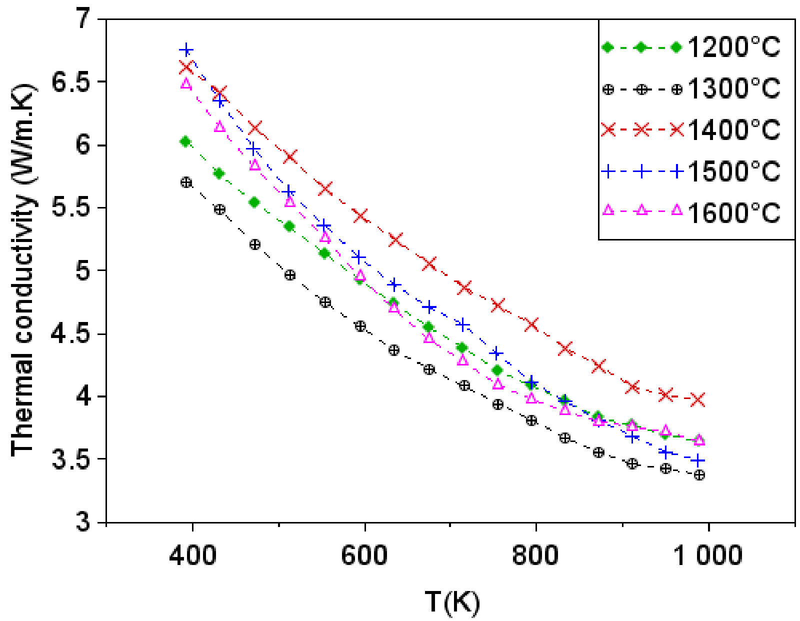


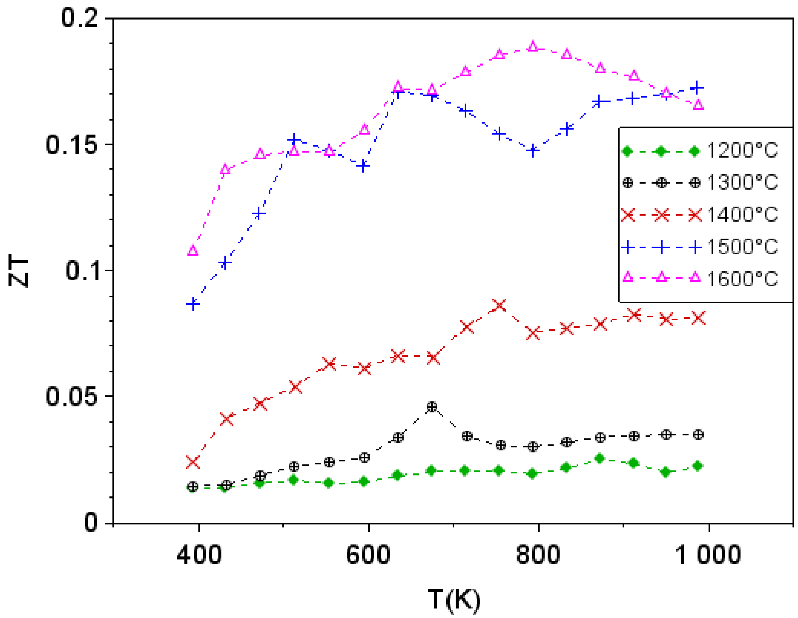




with increasing sintering temperature

- Electrical conductivity increases
- Seebeck coefficient value decreases with sintering temperature
- PF of 2 mW/m K^2 is reached at 100°C with a sintering temperature of 1600°C



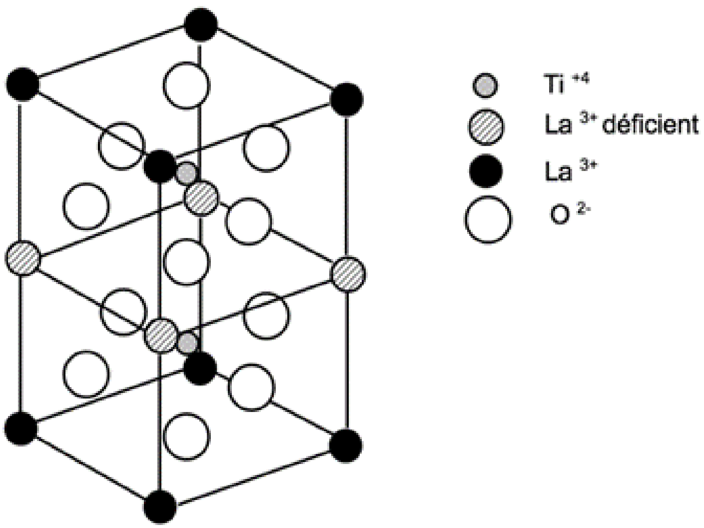


- Thermal conductivity evolution does not shown clear trend
- ZT reaches 0.15 @ 400K and 0.19 @ 800K
- No more post annealing under Ar/H_2
- Fast process (few minutes versus several hours)

E. Bsaibess et al. Eur. Phys. J. Spec. Top. (2022) 231:4195

Impact of SPS on thermoelectric oxide : $La_{0.66}Ti_{0.95}Al_{0.05}O_3$

$La_{0.66}TiO_3$



Abe et al (1974) Mat. Res. Bull. 1974

A-deficient perovskite

c parameter doubling

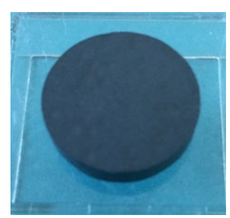
Stabilization with Al

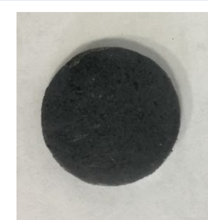
$La_{0.66}Ti_{0.95}Al_{0.05}O_3$

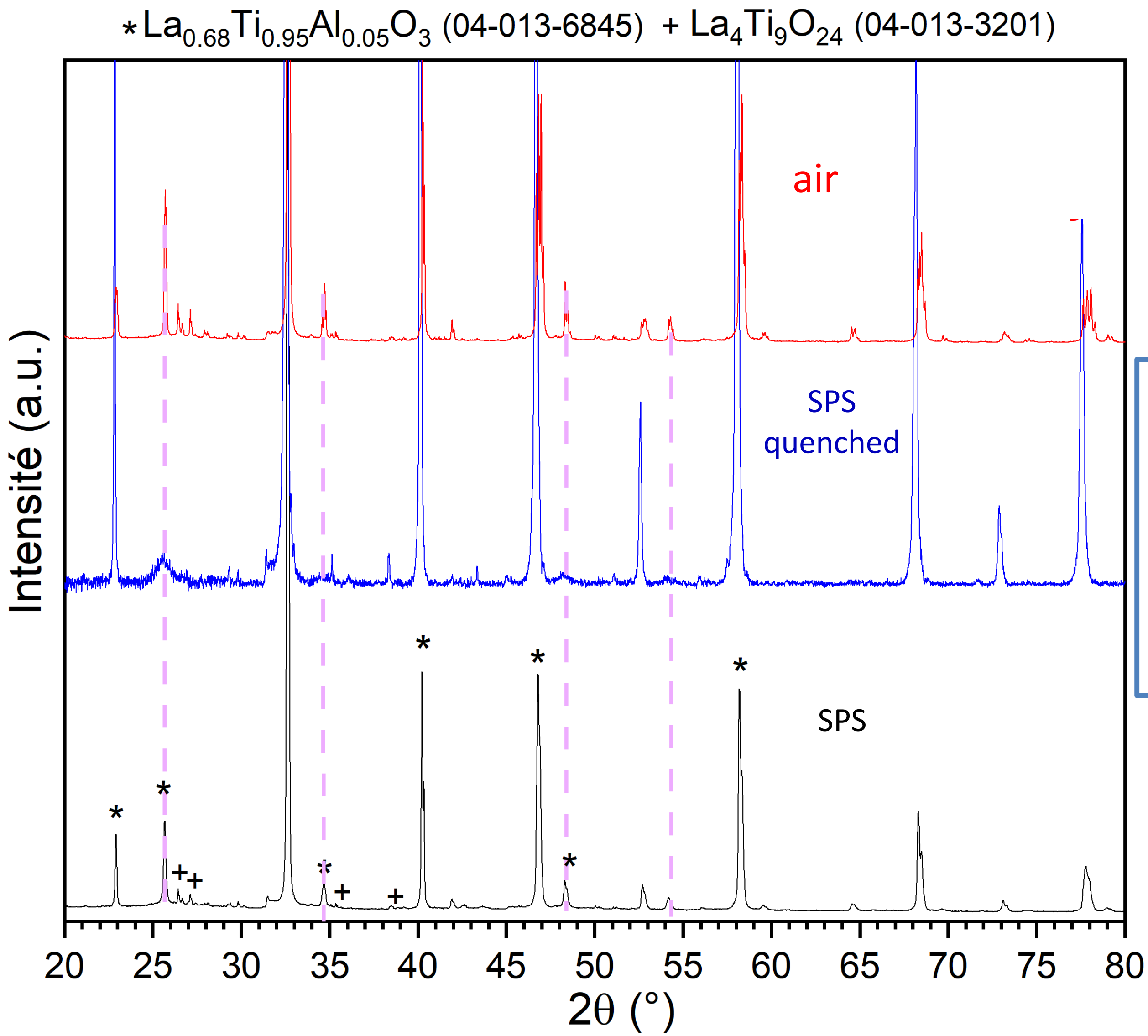
→ Thermal conductivity decreases

15

	air	air + annealing	Ar/H2	SPS	SPS quenched
Sintering temperature	1400°C	1400°C	1400°C	1300°C	1300°C
Time	8 h	8 h	8 h	5 min	0
Time and temperature of Ar/H_2 annealing		76 h 1300°C			
Density	90%	90 %	92 %	98%	98%





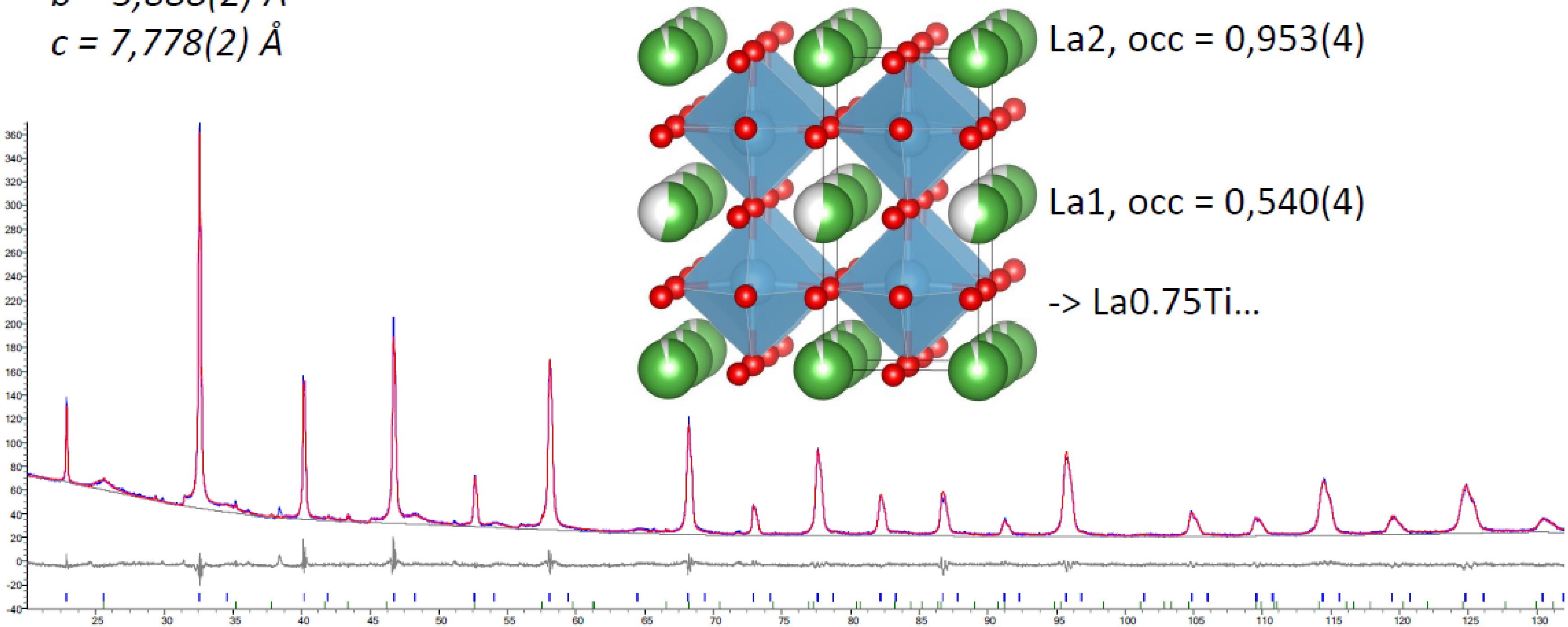


- Expected phase
- Impurities
- Quenched = low intensity of surstructure peaks

Rietveld fit of SPS Quenched

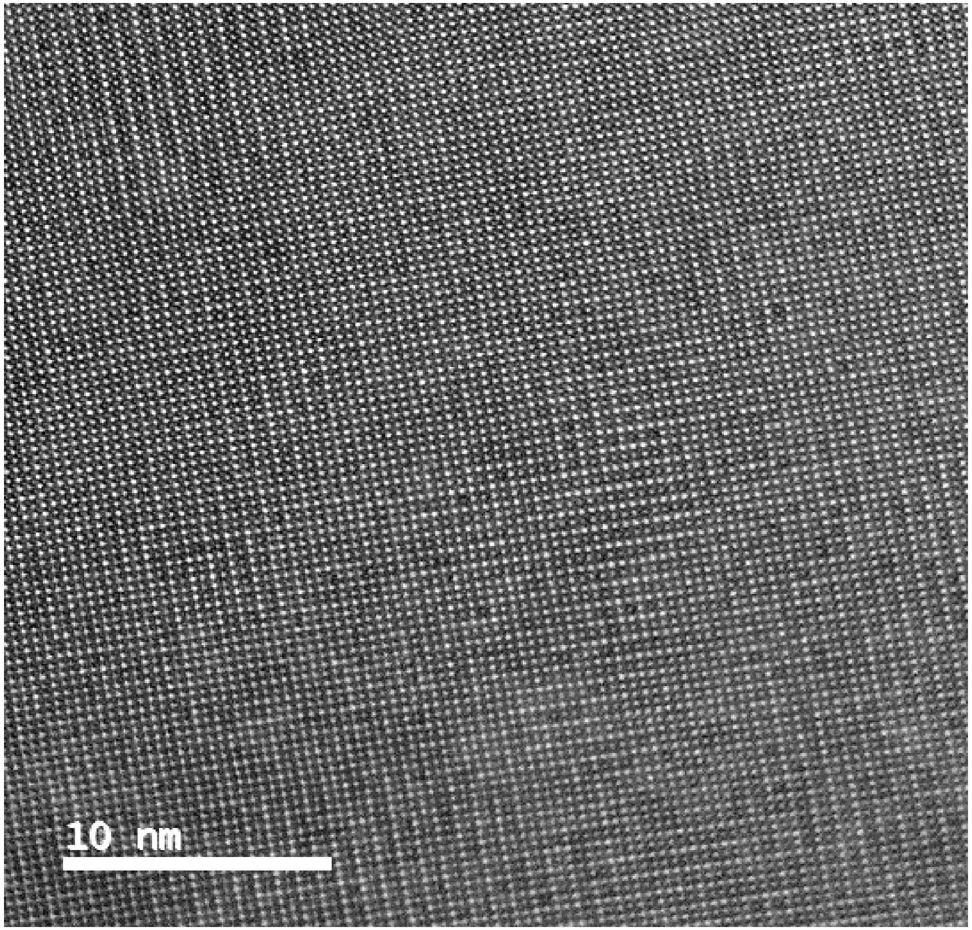
Pmmm
a = 3,888(2) Å
b = 3,888(2) Å
c = 7,778(2) Å

La, Ti parameters refined freely
O parameters fixed to published values

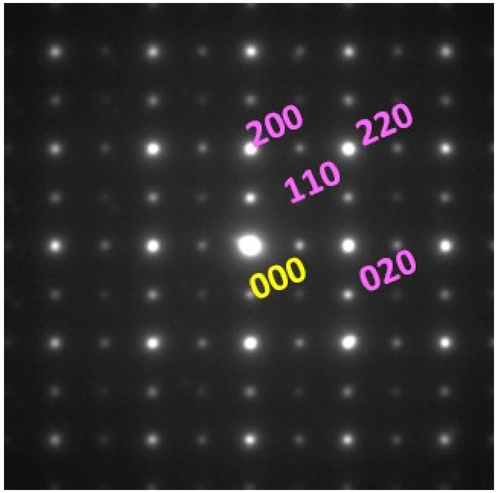


Pmmm is still good enough to produce a good Rietveld fit with reliable refined occupancies

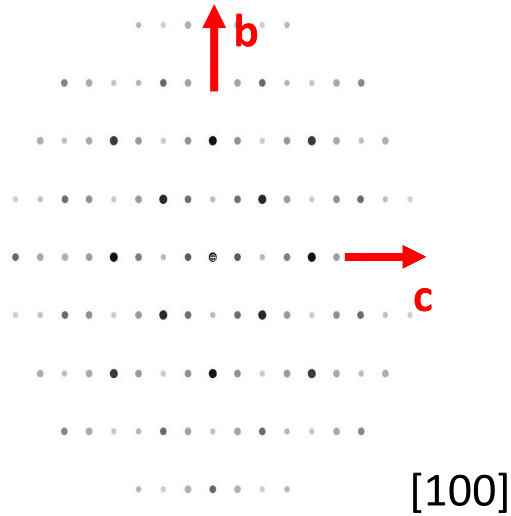
→ The sample is fully-ordered at the unit-cell level
→ The ordered domains have a size distribution centred around 6 nm

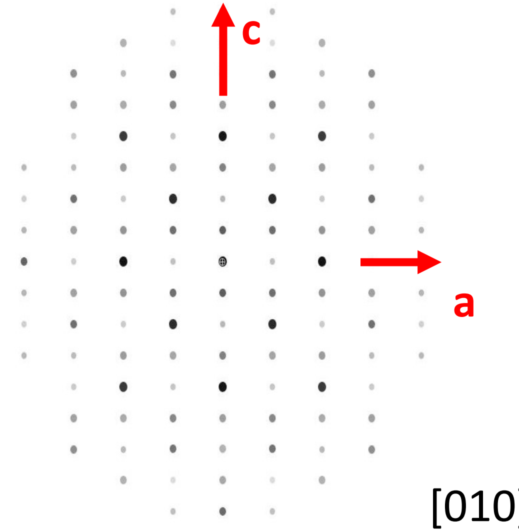


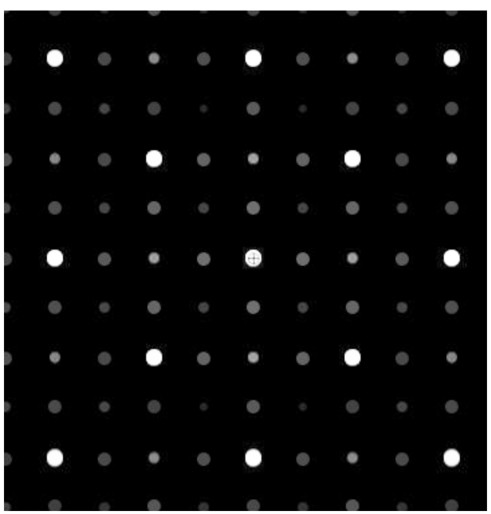
STEM-HAADF image at the atomic resolution of the quenched sample prepared as a thin lamella.



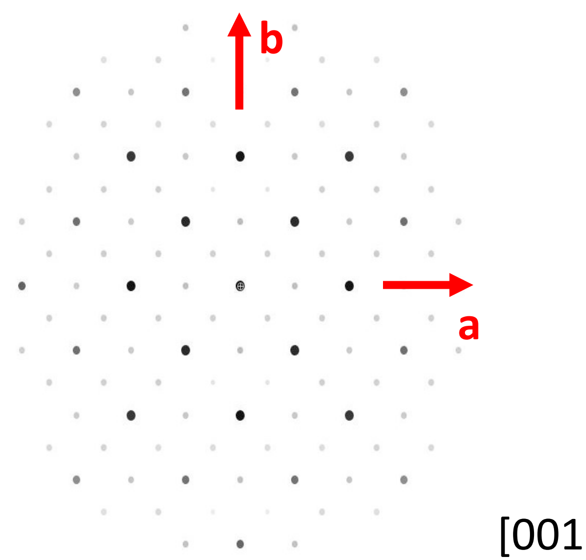
Selected Area Electron Diffraction pattern obtained, along the [100] zone axis familly ([100], [010], [001]).

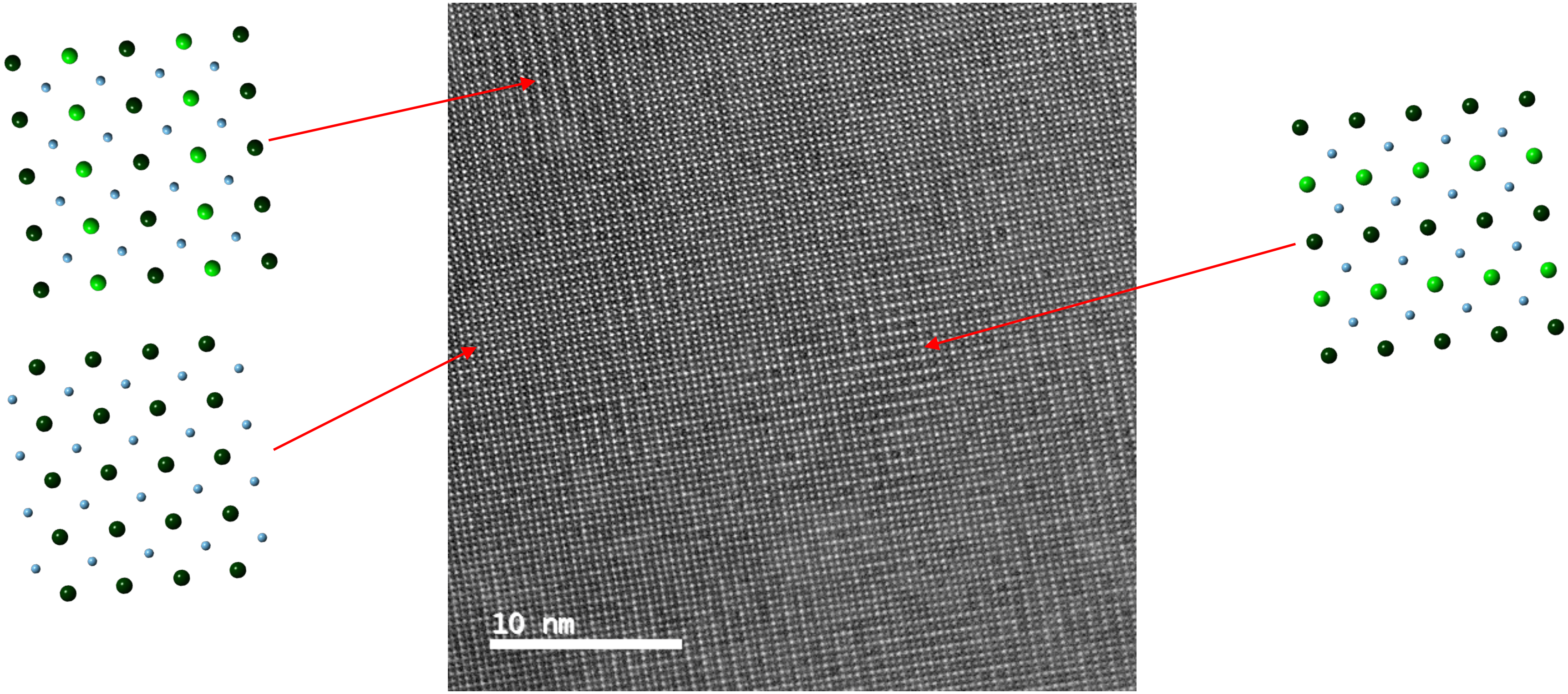






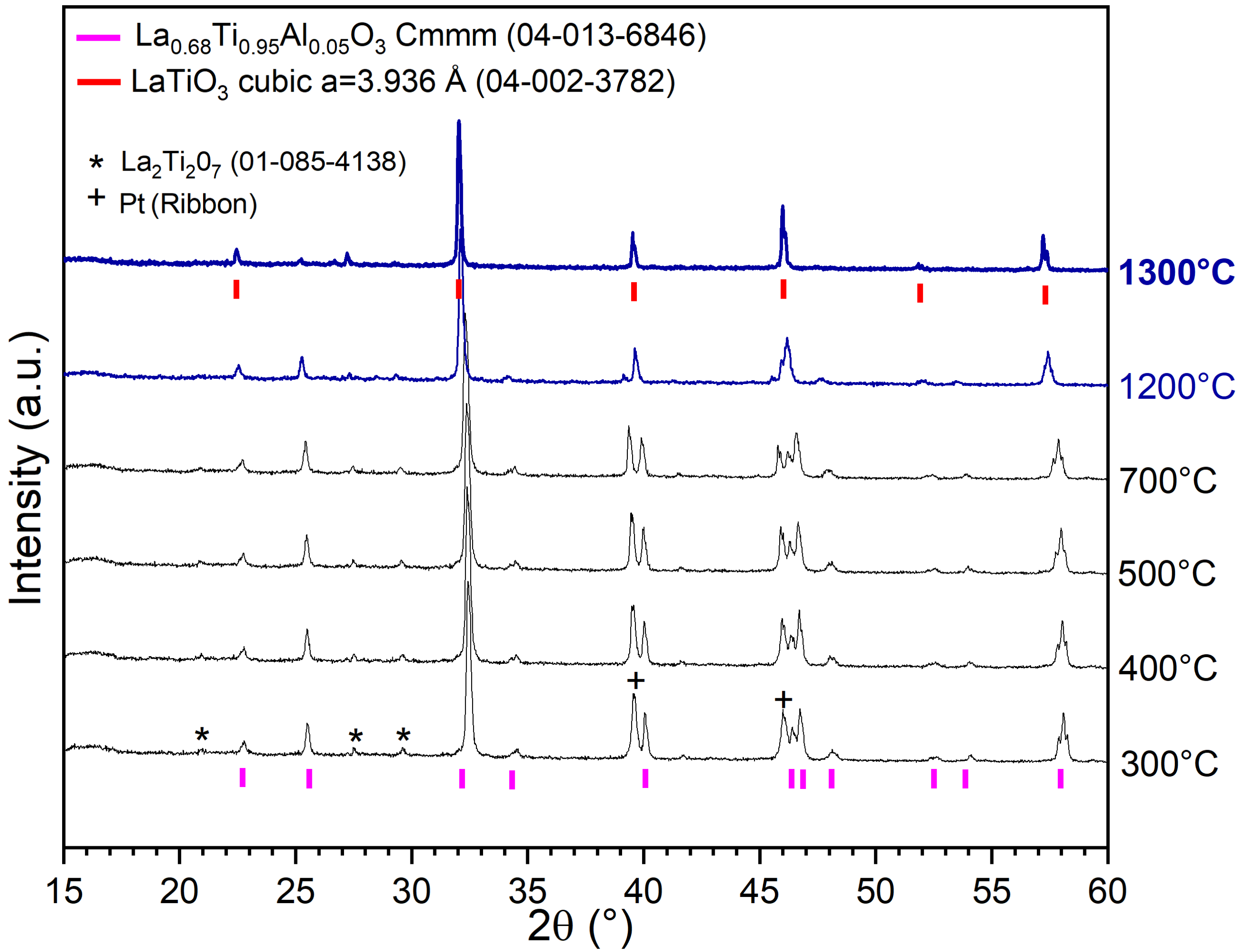
By superposition of the 3 simulated electron diffraction patterns we can reproduce an electron diffraction pattern with a very good match with the experimental SAED.



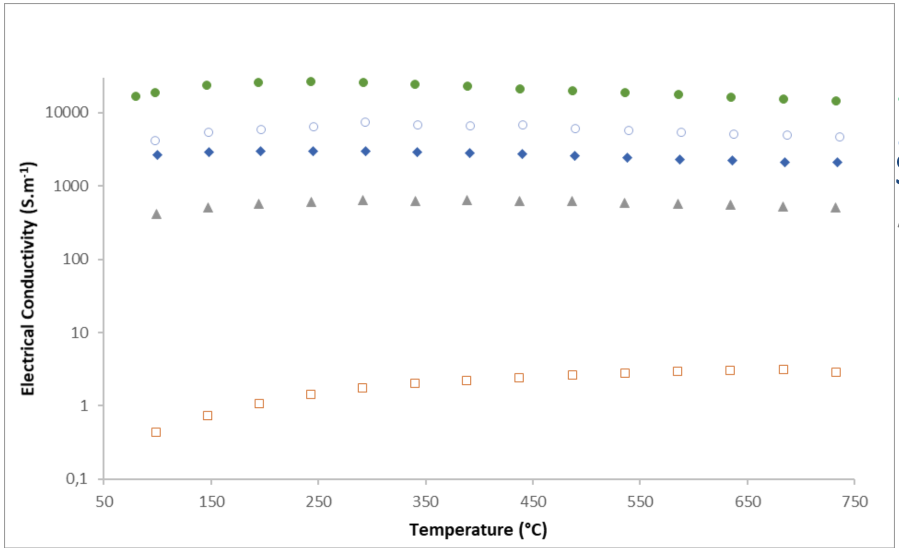


STEM-HAADF image at the atomic resolution of the quenched sample.

⇨ Presence of nanodomains



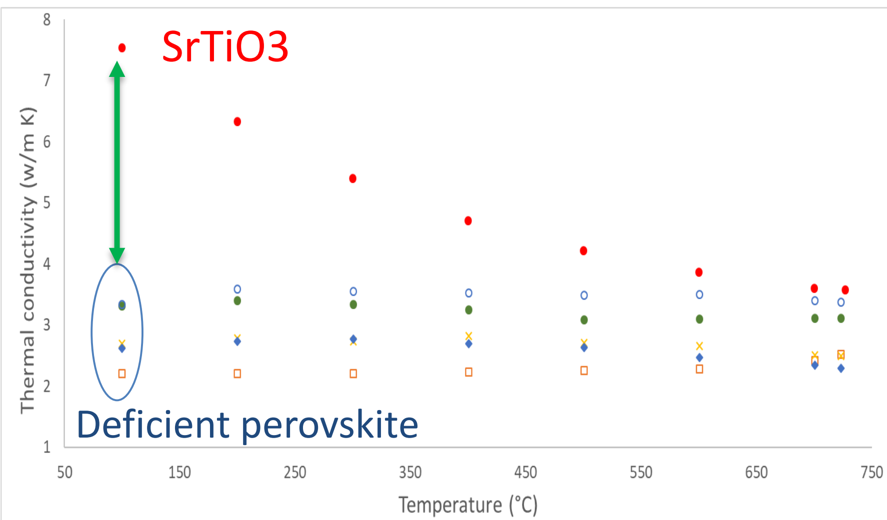
High temperature cubic phase



SPS-quenched
SPS
Sintering Ar/H_2
Annealing Ar/H_2

air

Best PF is obtained for the quenched sample

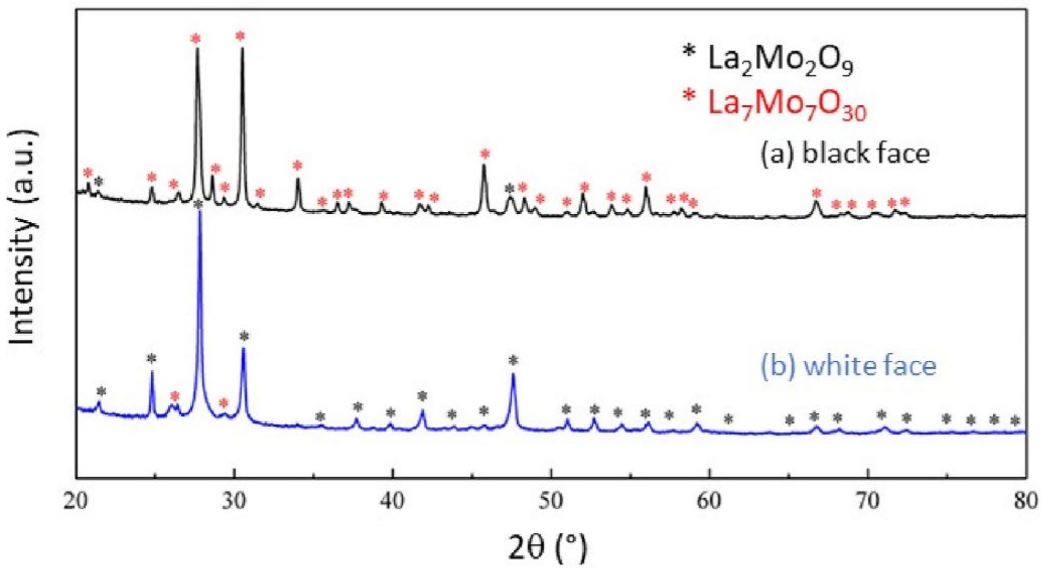


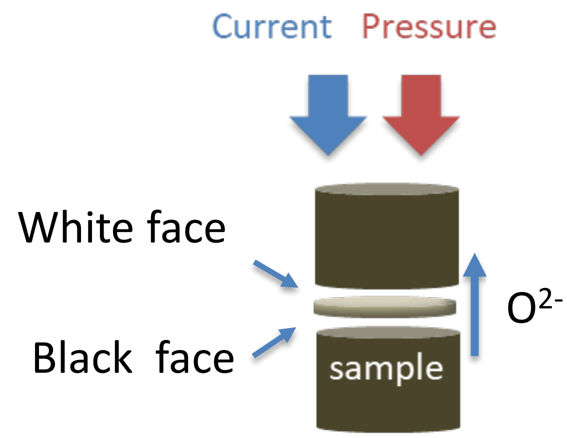
The thermal conductivity is divided by 2 at 100°C in comparison of $SrTiO_3$

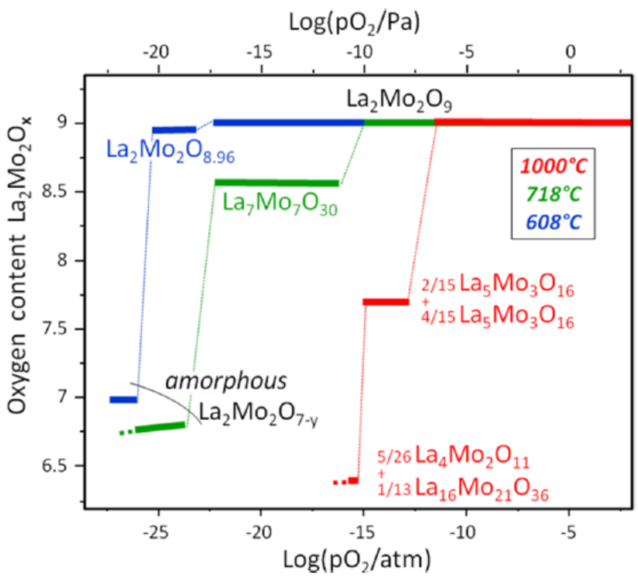
ZT of 0.12 is reached at 1000K

Impact of SPS on Ionic conductor :$La_2Mo_2O_9$

SPS 700°C , 5 min, 90 MPa



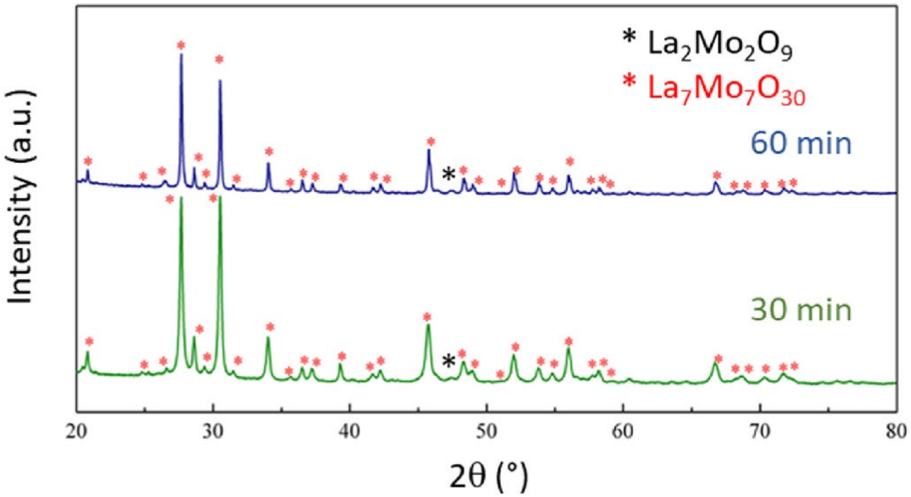


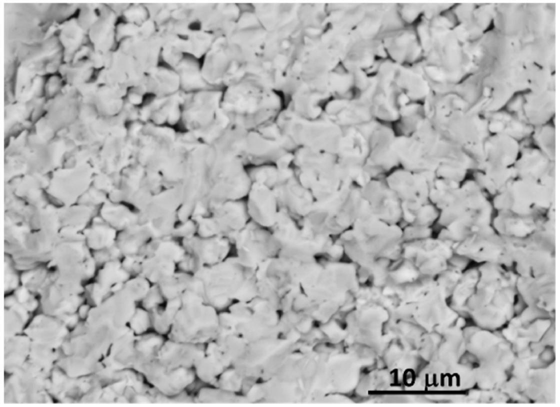


Buvat et al. Inorg. Chem. 55 (2016) 2522

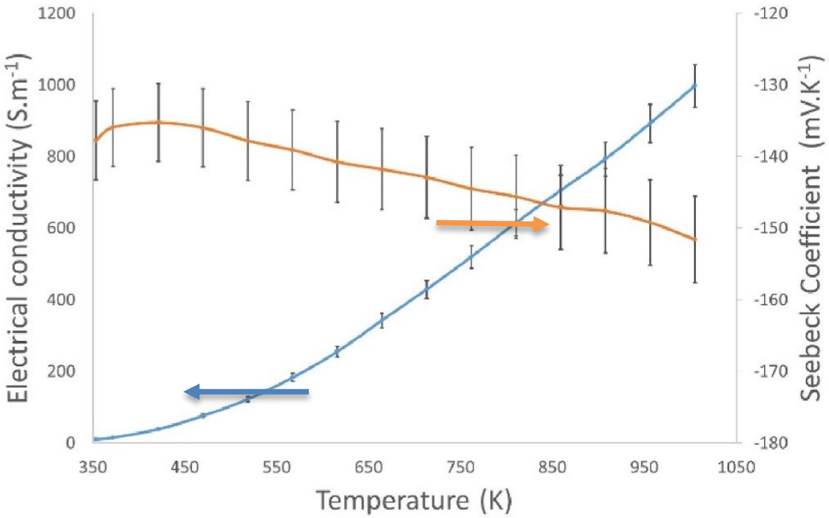
$La_2Mo_2O_9$ in situ transformation in reduced phase $La_7Mo_7O_{30}$

SPS 700°C , 90 MPa





89 % relative density



Thermoelectric properties evaluation of the reduced phase $La_7Mo_7O_{30}$
ZT= 0,04 @ 1000K

Giovannelli et al. Ceramics International 49 (2023) 11921

Conclusion

- Oxygen annealing allows recovering piezoelectric material in KNN
- Reducing atmosphere leads to good thermoelctric properties without Ar/H_2 annealing
- Quenched $La_{0,66}Ti_{0,95}Al_{0,05}O_3$ sample exhibits nanodomains
- In situ transformation of $La_2Mo_2O_9$
- Obtention of $La_7Mo_7O_{30}$ ceramic

SPS could be advantage or disadvantage depending on what we are looking for but obviously new opportunities