Millisecond-Resolved Total Scattering of Rapid Transformations in Electrochemical Flash Sintering

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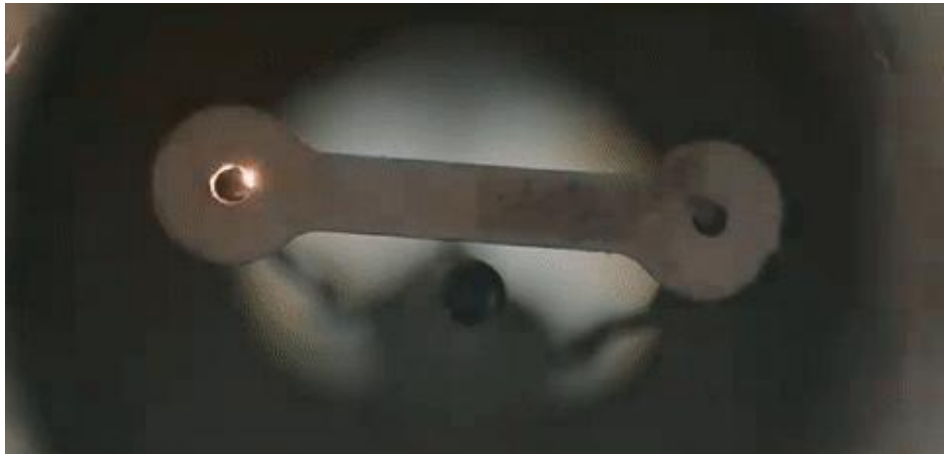
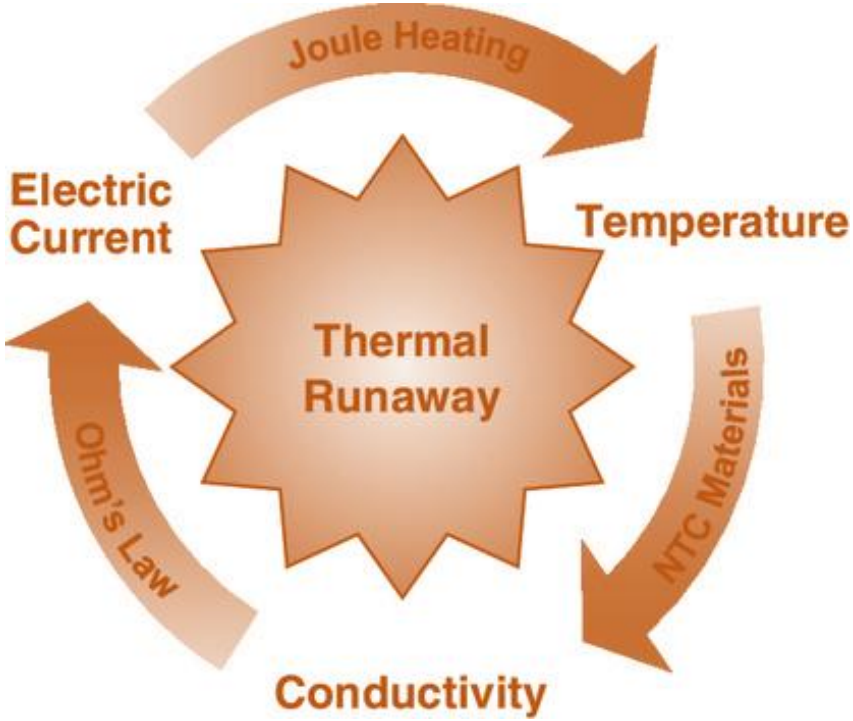
Flash Sintering

Non-equilibrium densification reaction in 1-2 seconds



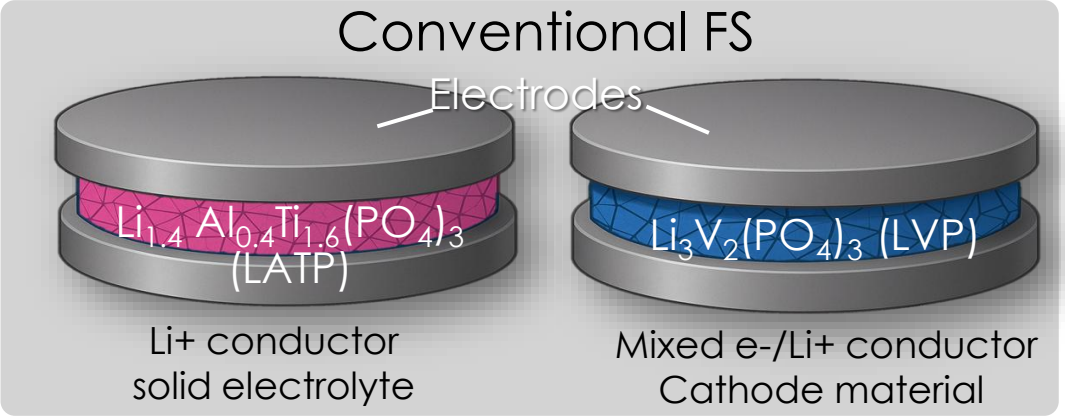


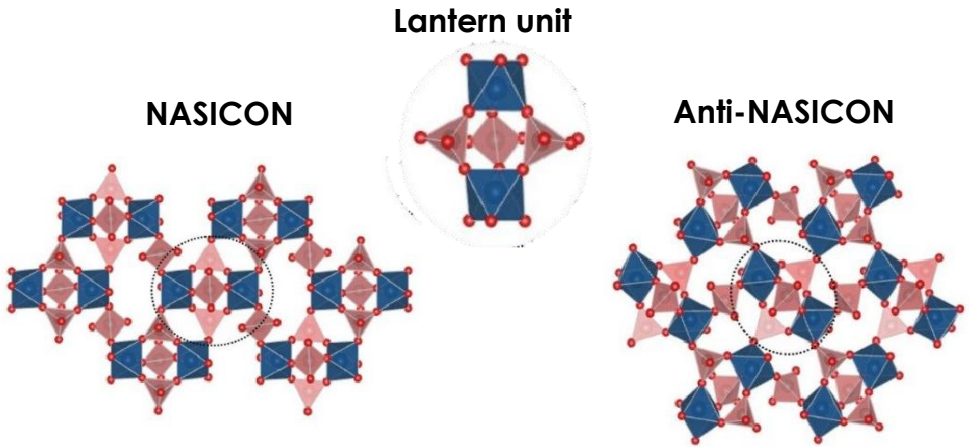
Flash Sintering for battery synthesis

Main challenge:
hotspots, cracks, phase inhomogeneity

Approaches:
single components vs composites / multilayers)

Objective:
Understand material-specific flash response





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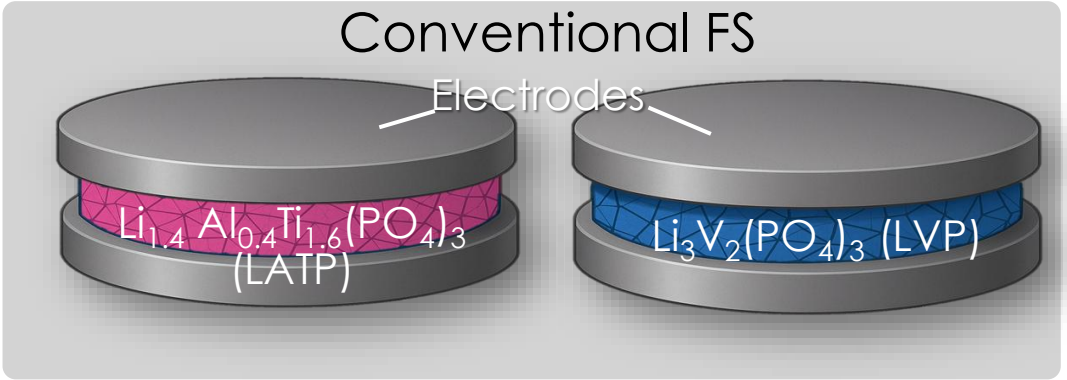
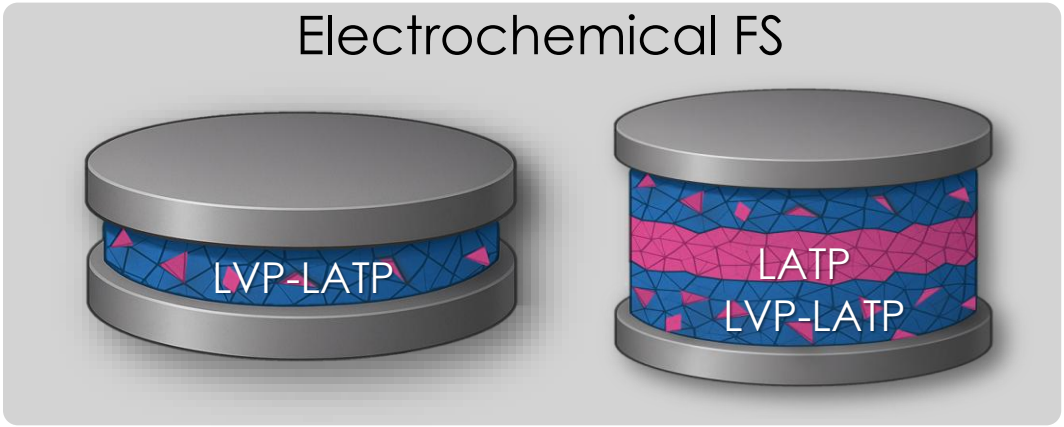
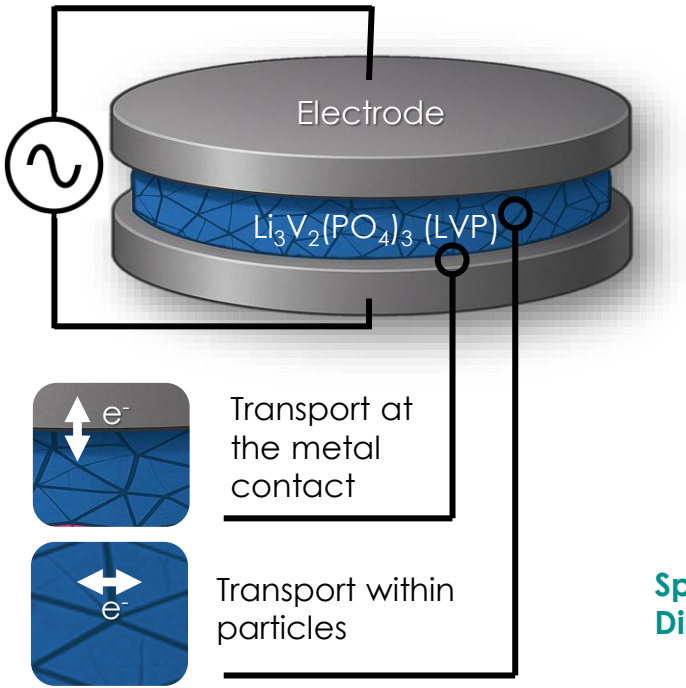
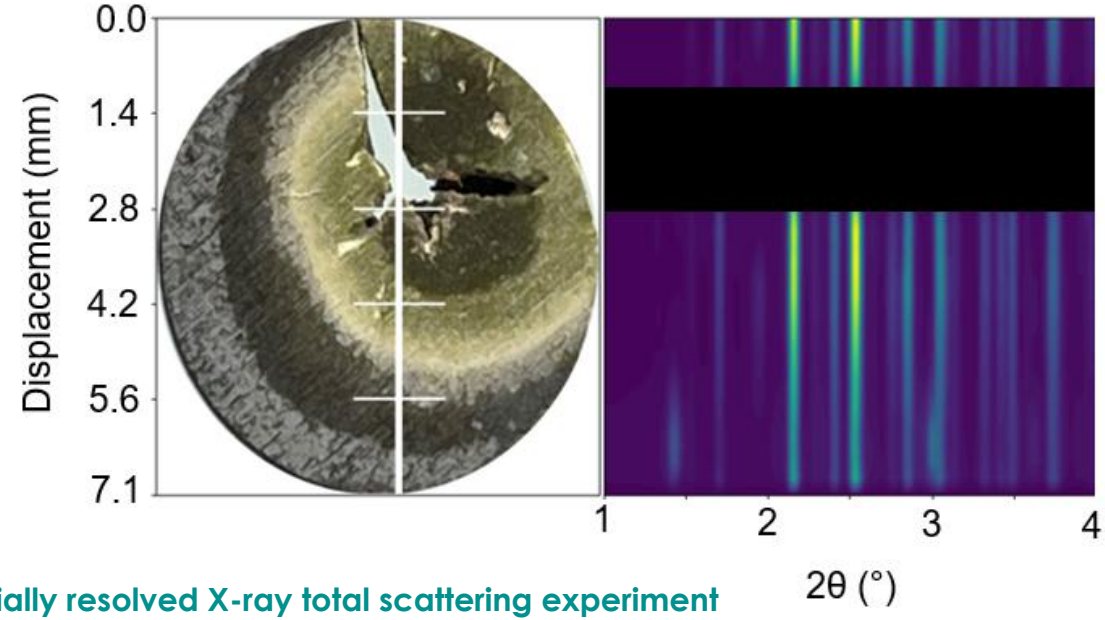




Conventional FS LVP





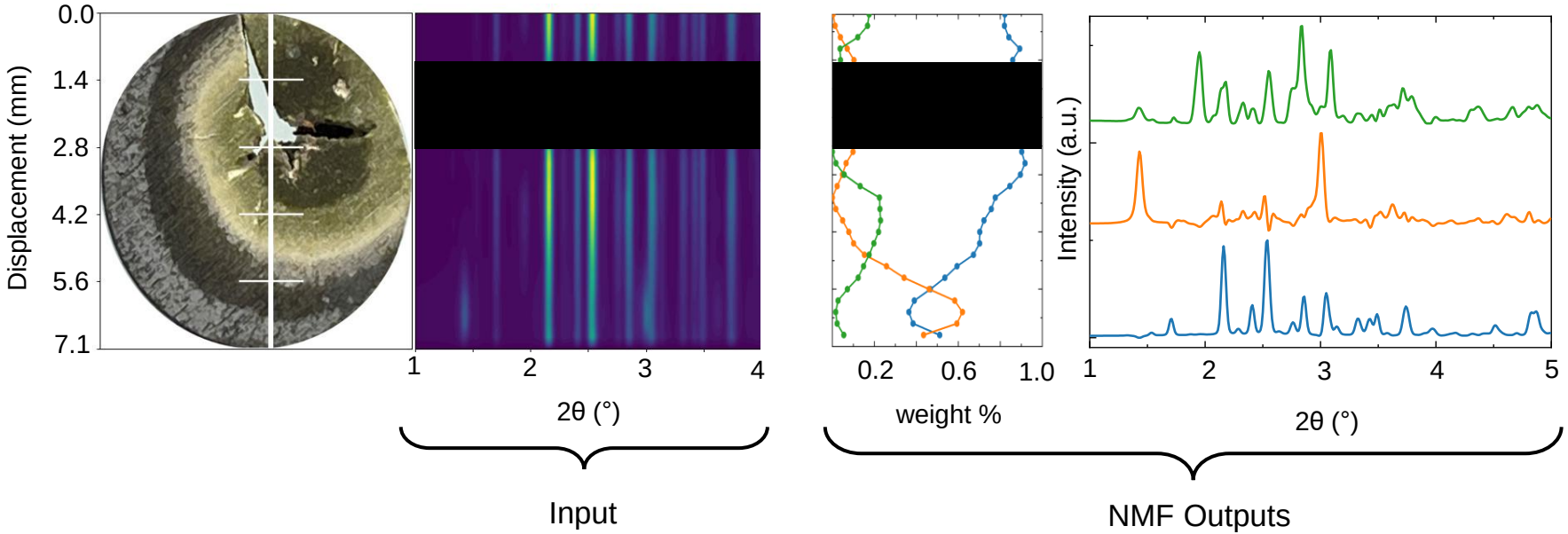
Spatially resolved X-ray total scattering experiment
Diamond Light Source, UK XPDF I15-1 Beamline

Conditions:
- E = 76.69keV, λ = 0.161669 Å
- Beam: 700 µm x 10 µm
- Transmission mode
- 2D Detector: Perkin Elmer XRD 4343 CT

Conventional FS LVP

PDF IN THE CLOUD

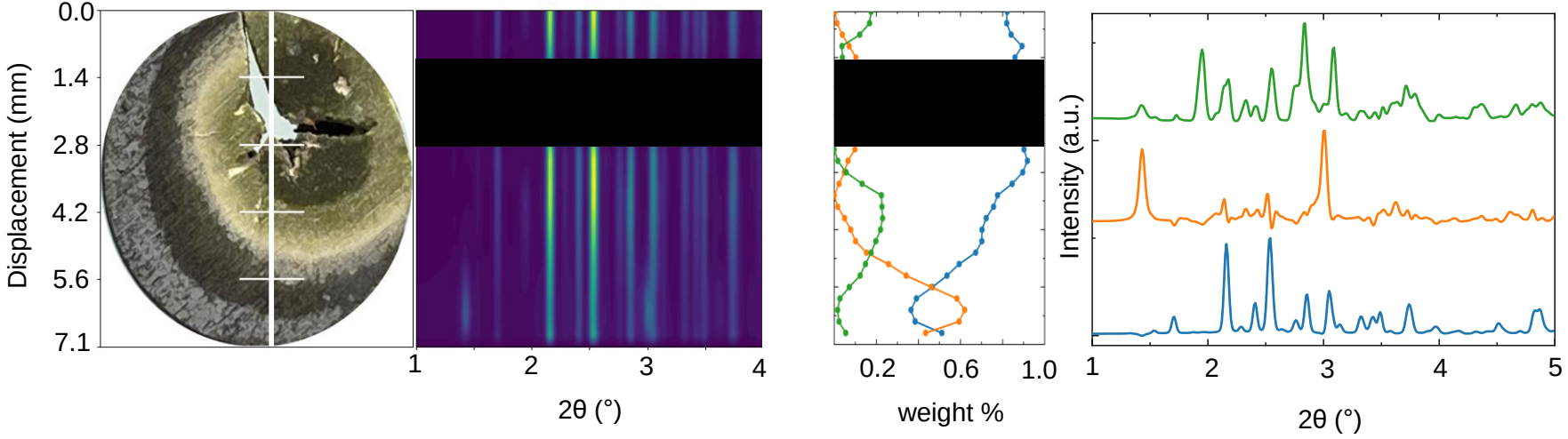
https://pdfitc.org/NMF

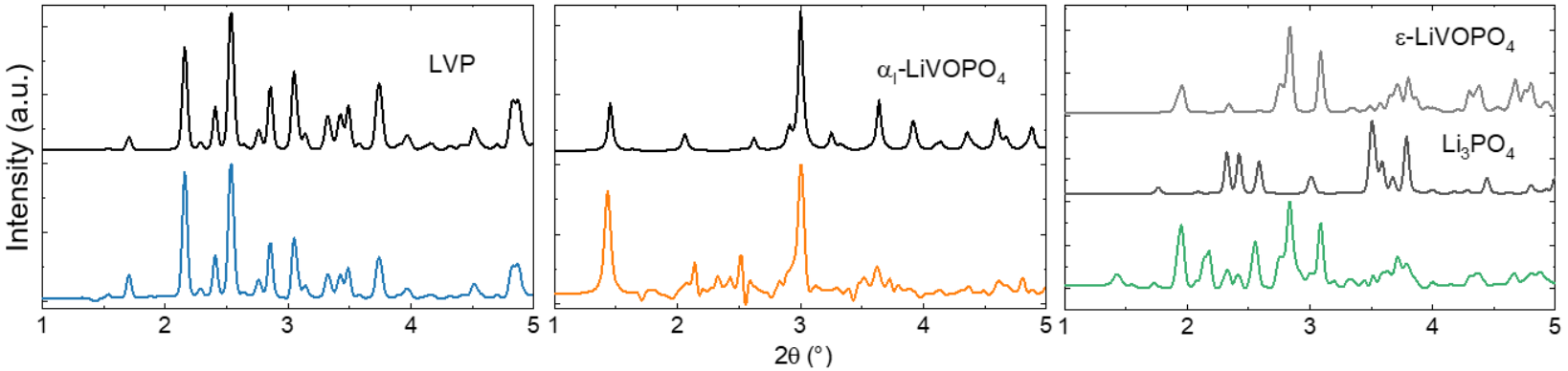


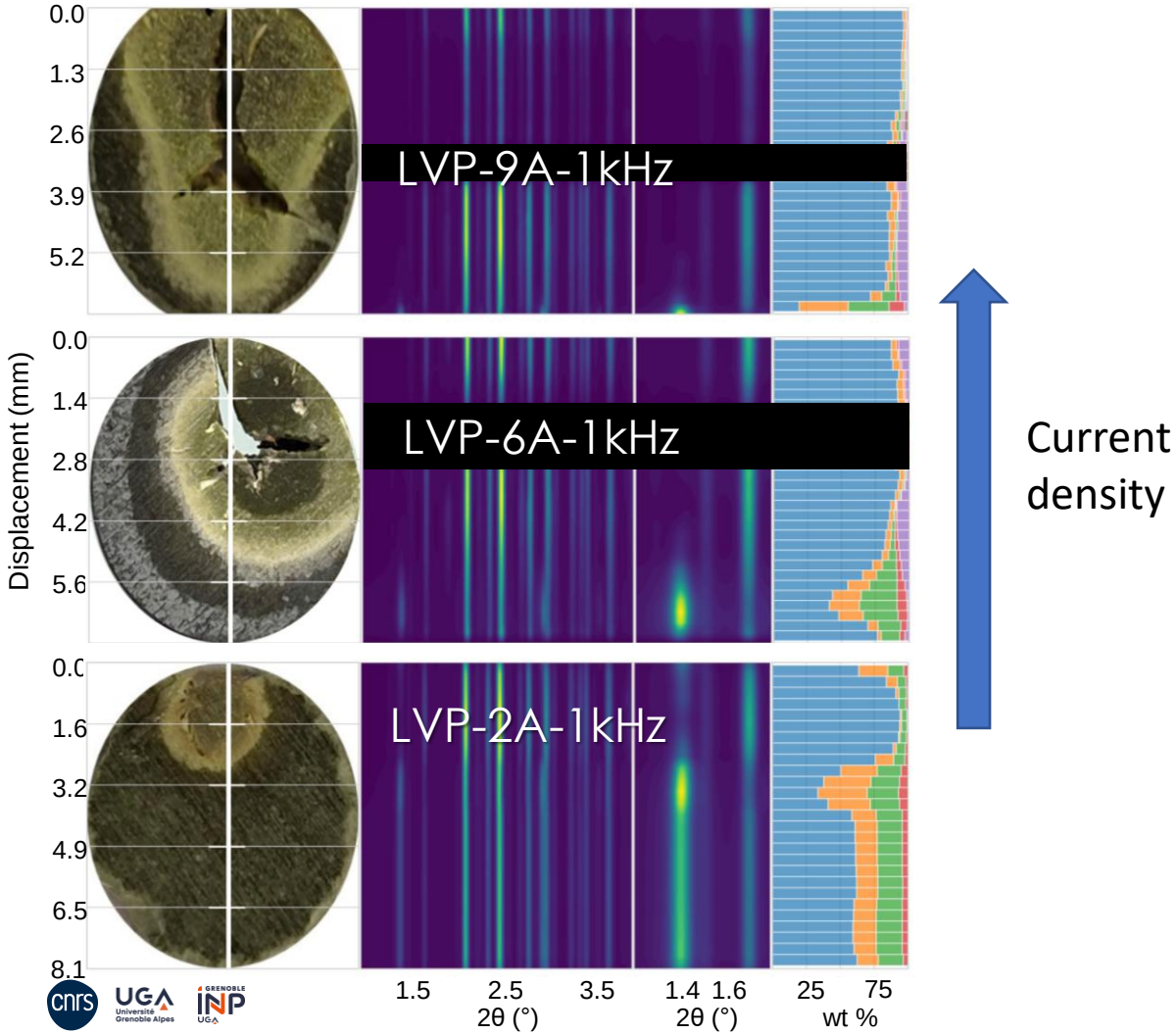
Conventional FS LVP

PDF IN THE CLOUD

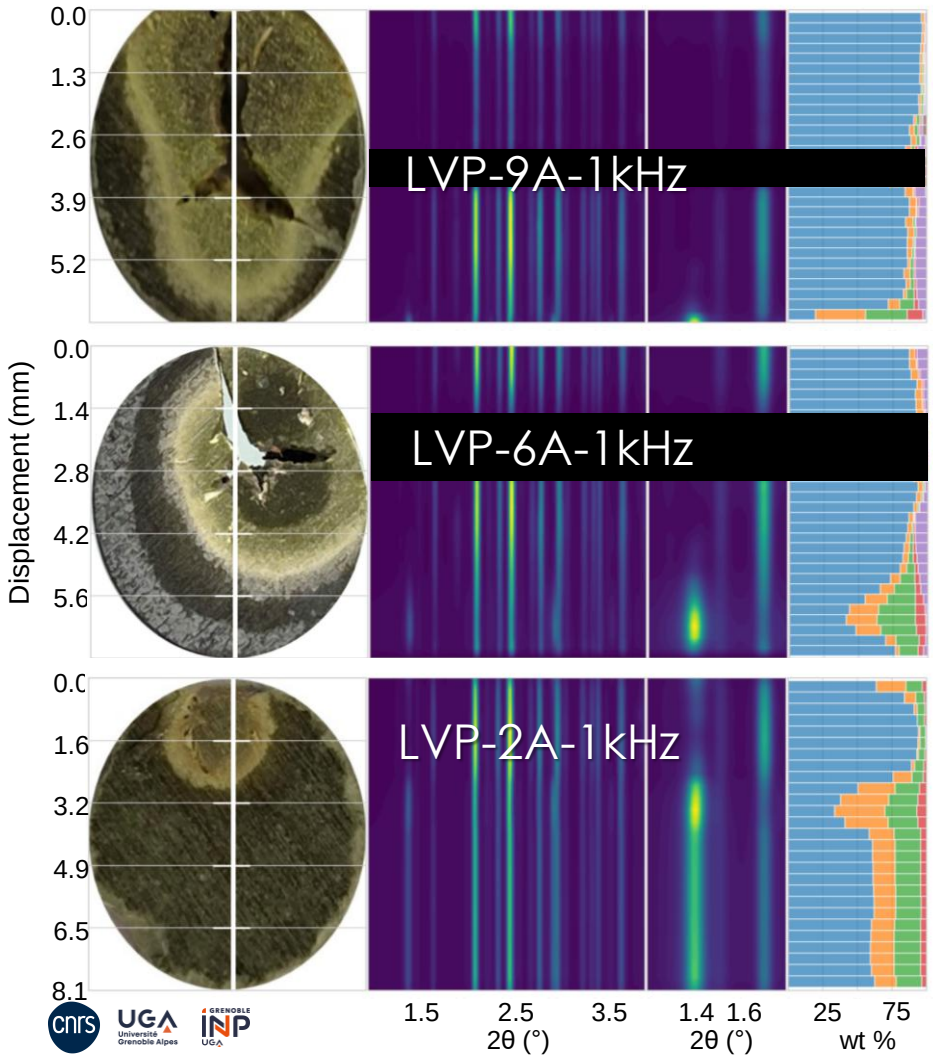
https://pdfitc.org/NMF

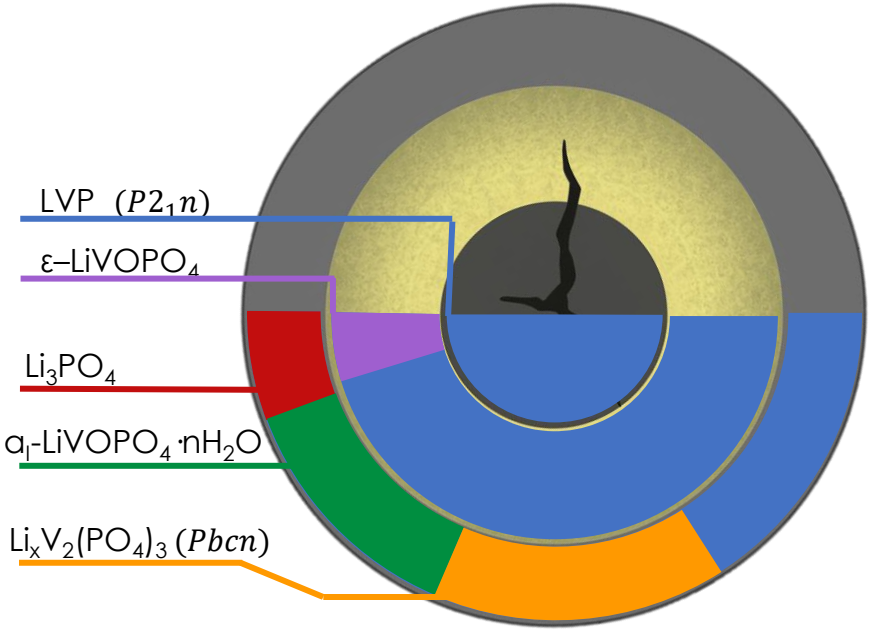




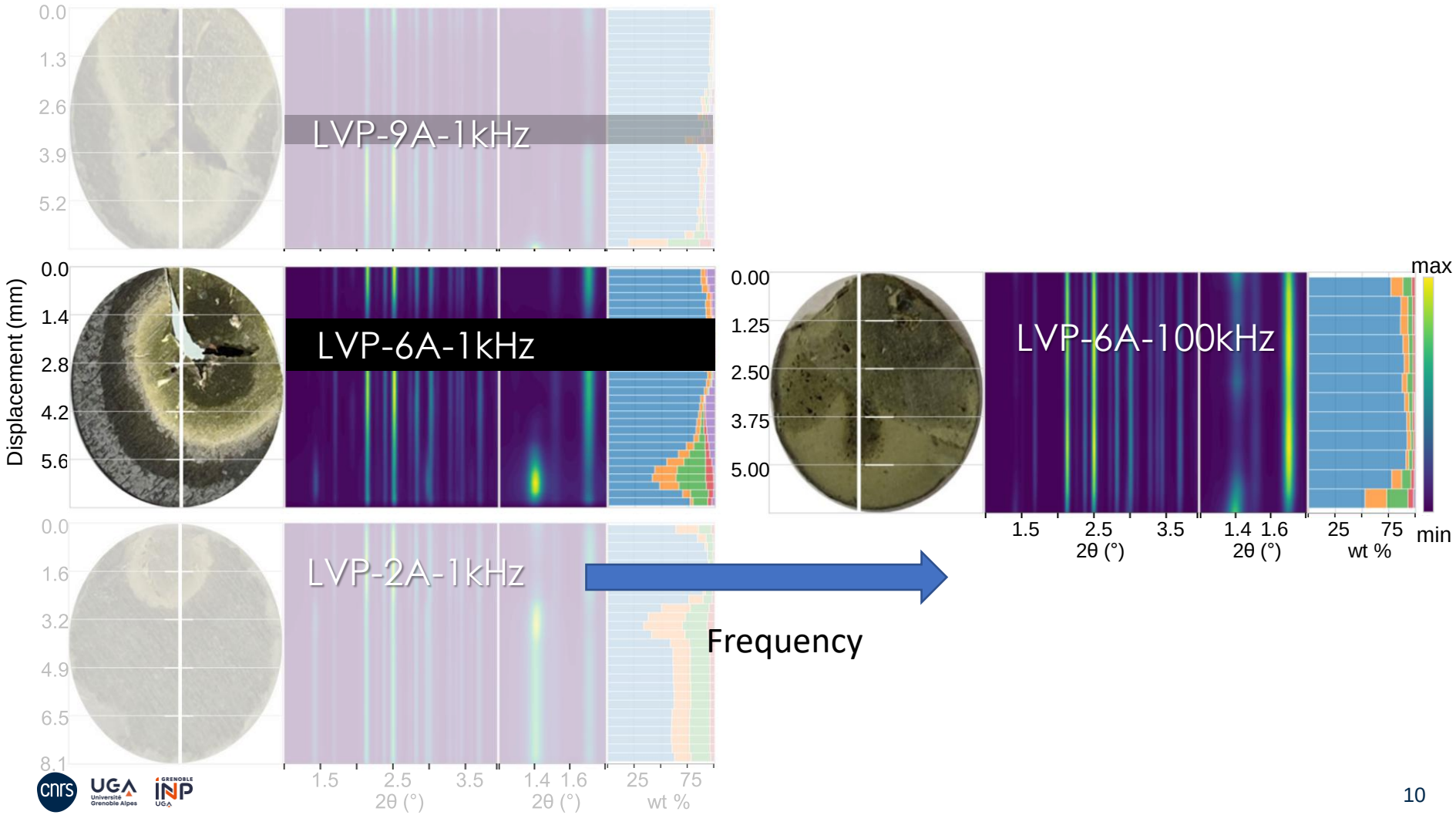


Current density

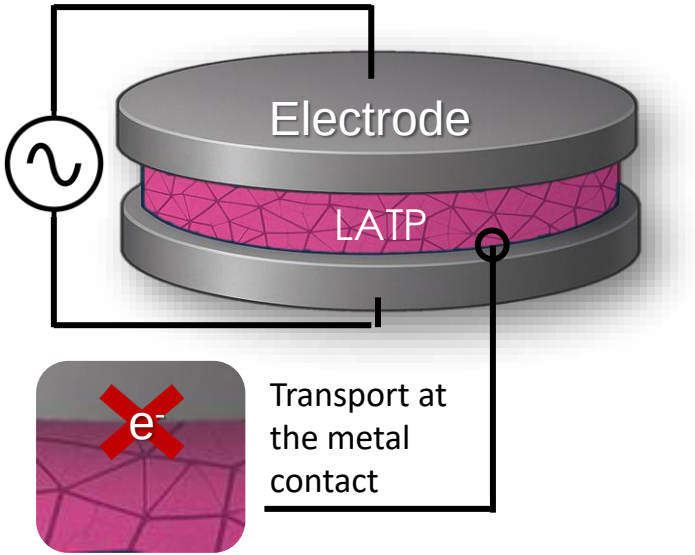


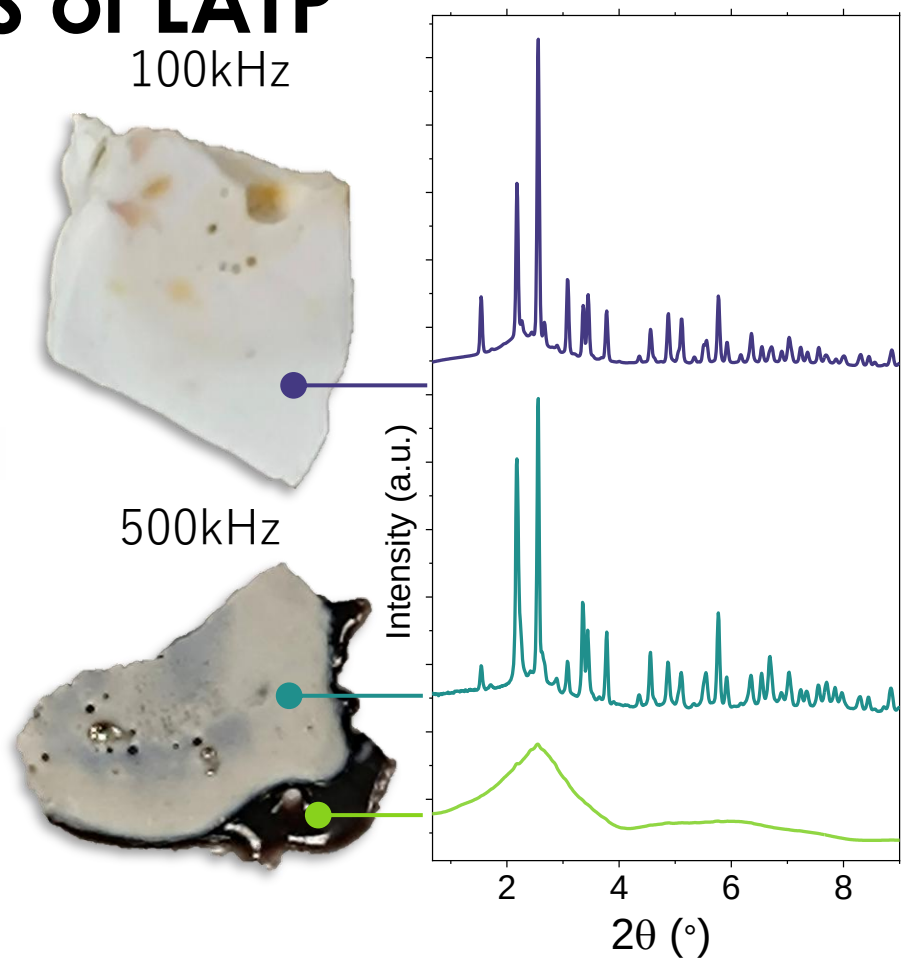


LVP decomposition is driven by Li^+ volatility, leading to **LVOP** formation

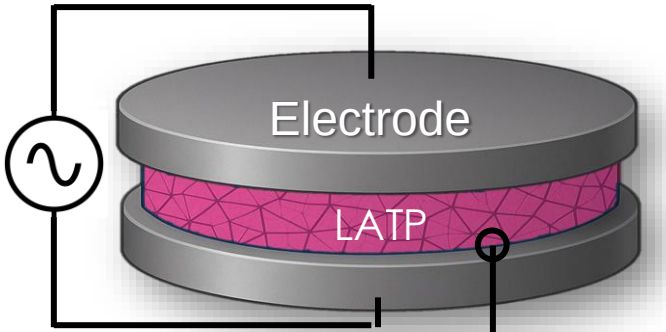

0.0
1.3
2.6
3.9
5.2
LVP-9A-1kHz
Displacement (mm)
0.0
1.4
2.8
4.2
5.6
LVP-6A-1kHz
0.00
1.25
2.50
3.75
5.00
LVP-6A-100kHz
max
min
0.0
1.6
3.2
4.9
6.5
8.1
LVP-2A-1kHz
1.5
2.5
2θ (°)
3.5
1.4 1.6
2θ (°)
25
75
wt %
Frequency

Conventional FS of LATP



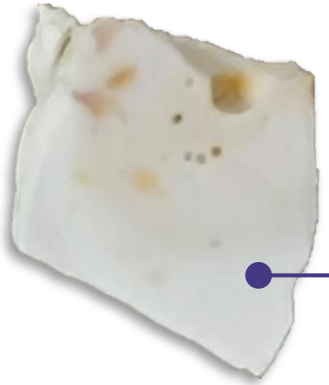


Conventional FS of LATP

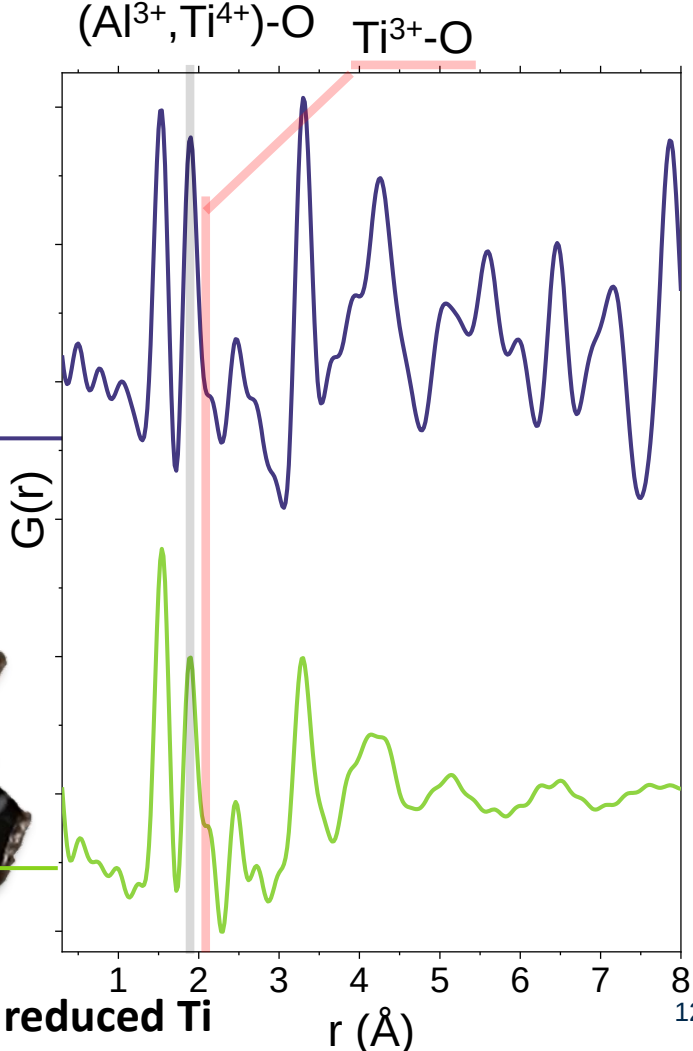


Transport at the metal contact

100kHz

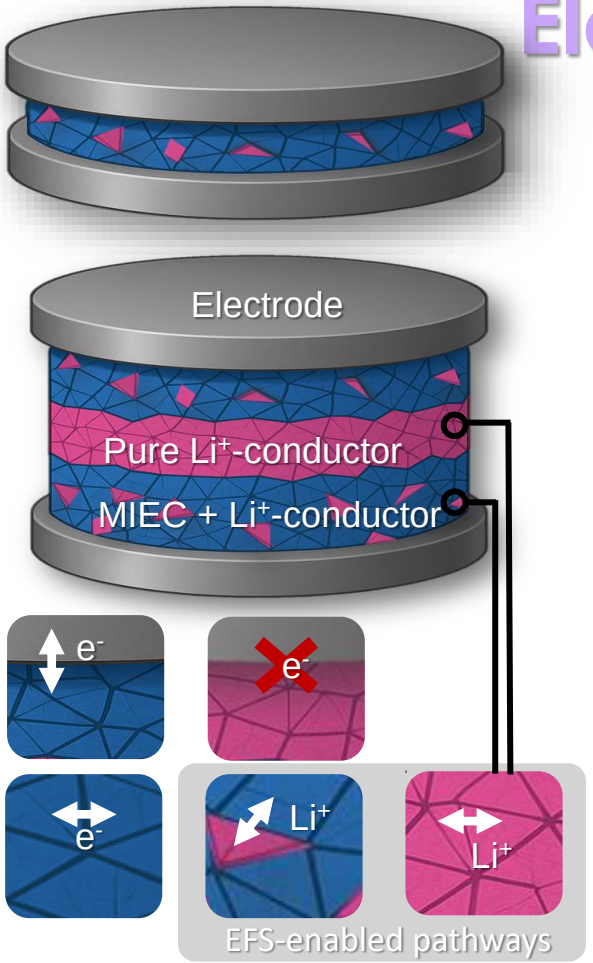


500kHz



Melt: local structure of LATP with partially reduced Ti

Electrochemical Flash Sintering



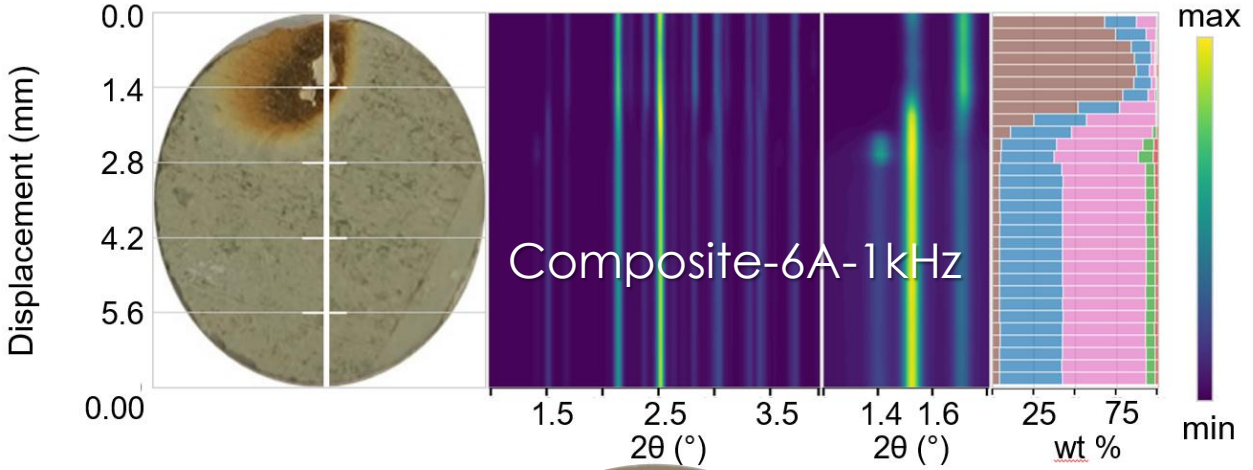
- Utilizing $e^- \leftrightarrow Li^+$ coupling can unlock new EFS pathways

- Promising, but reactions are fast and difficult to control.

- *In-situ* total scattering/PDF as a route to understand EFS reactions and densification mechanism(< 2 s)

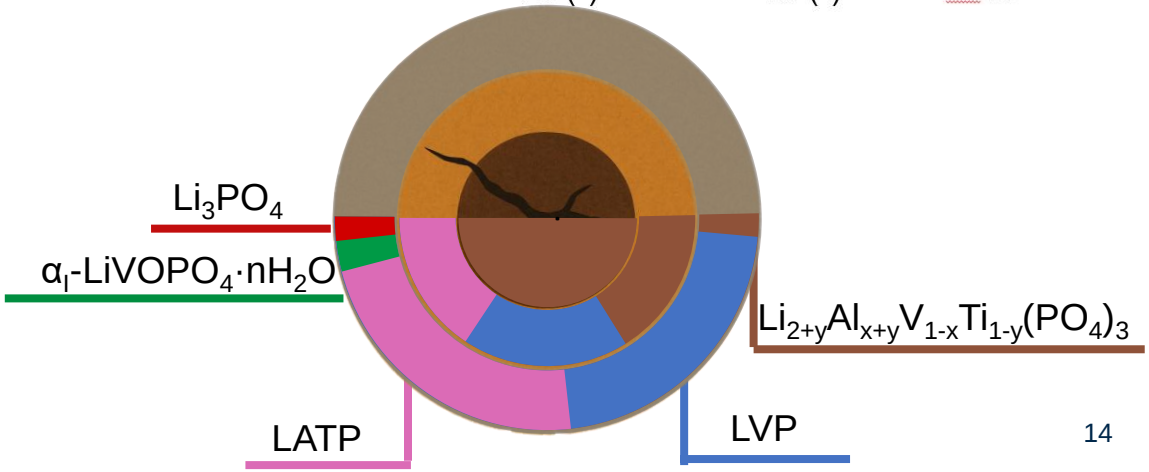
Electrochemical Flash Sintering as a new tool to obtain all solid-state *batteries* in few seconds – FLASHBAT (ANR, Bouchet LEPMI)

Electrochemical FS of Composite

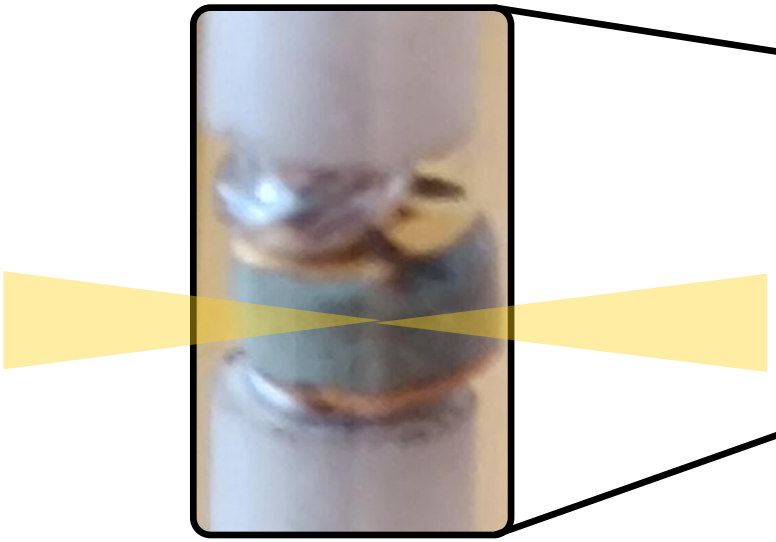


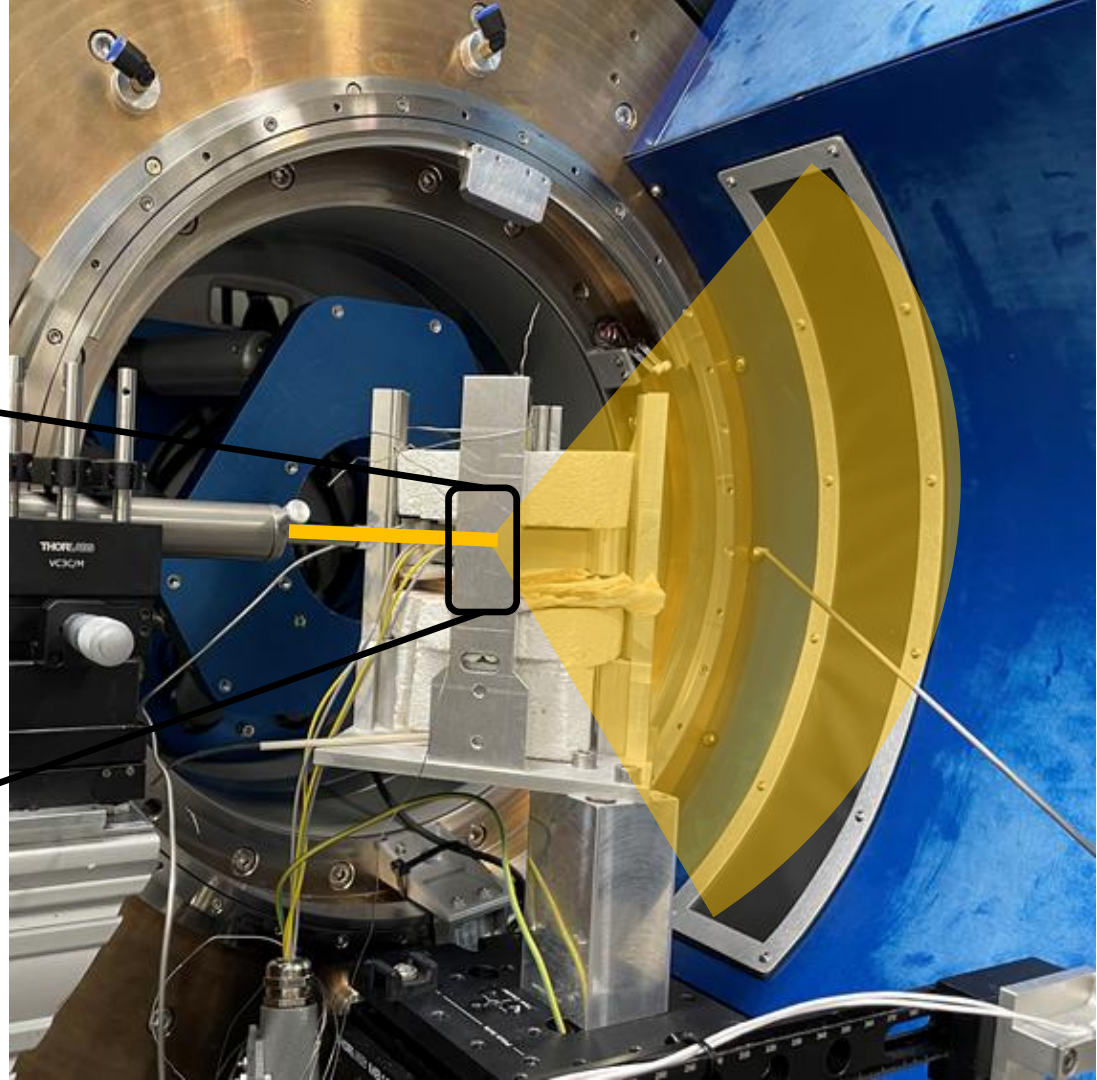
-Conventional co-sintering:
full reaction at 700°C

-EFS suppresses LVP-LATP reaction outside hotspot core

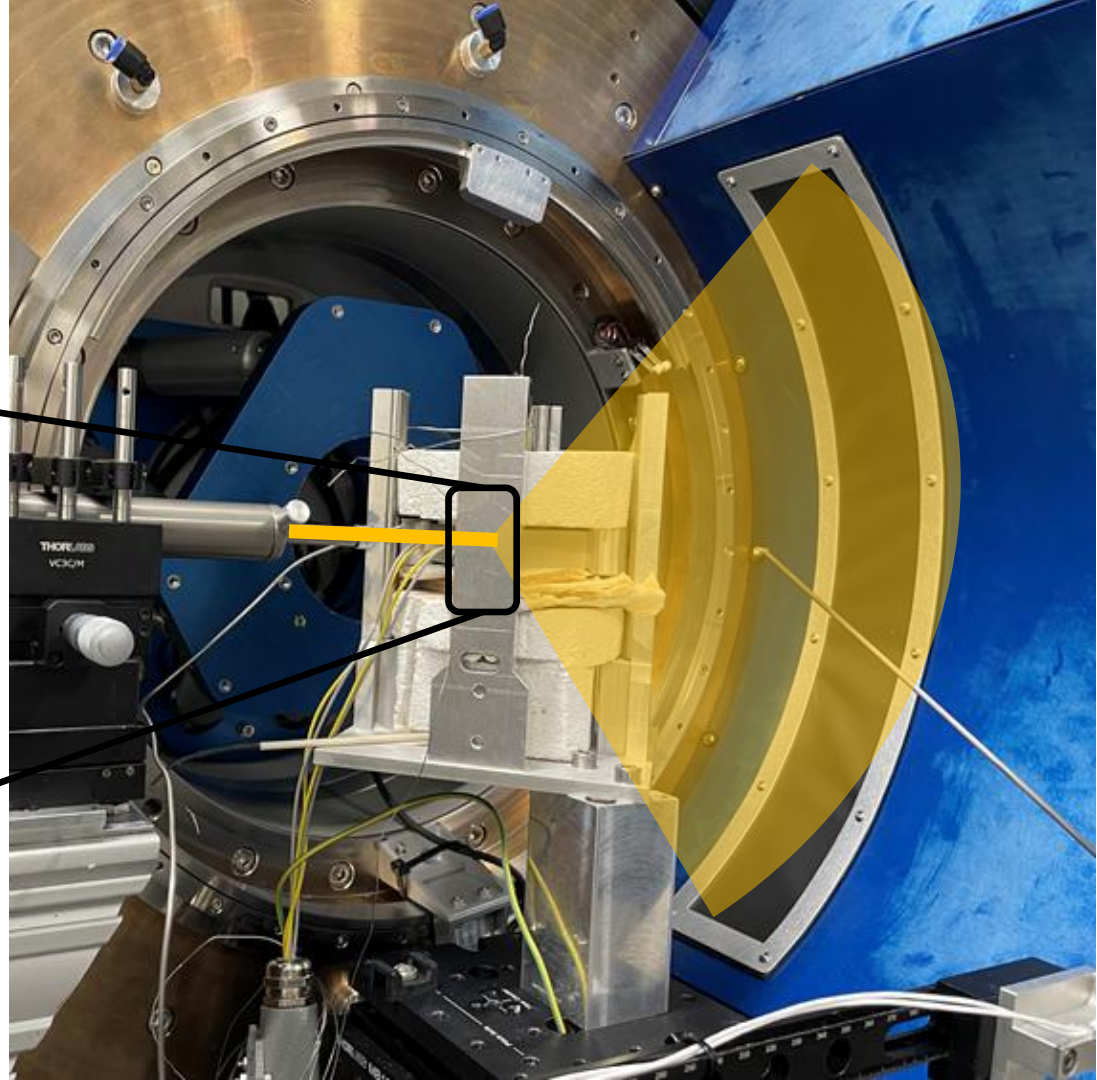


In-Situ FS Cell



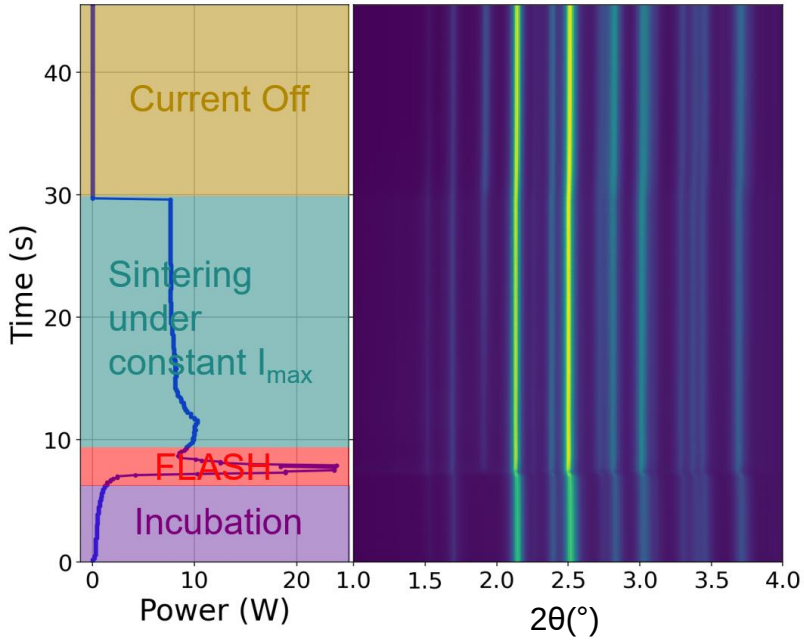


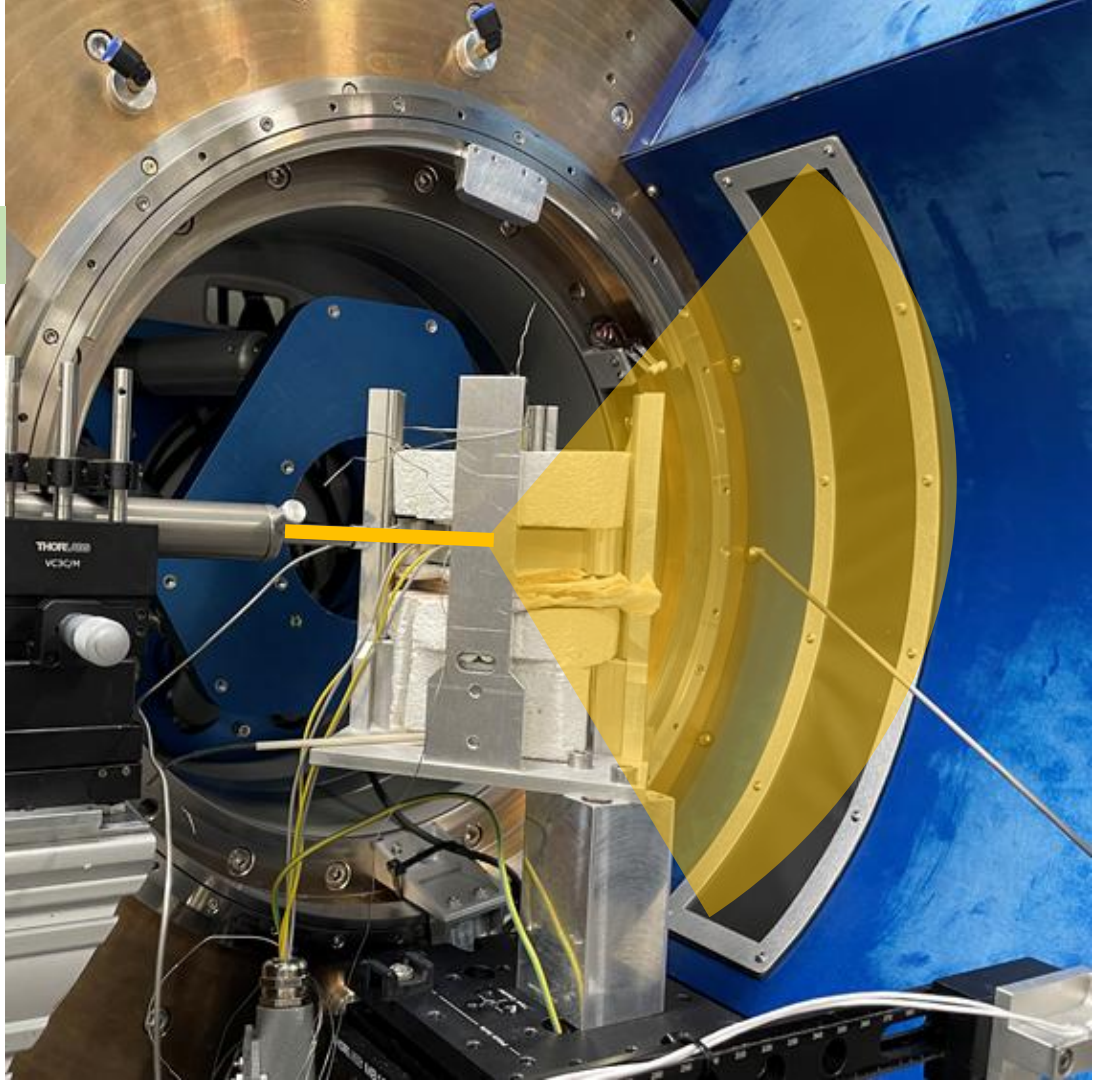
In-Situ FS Cell



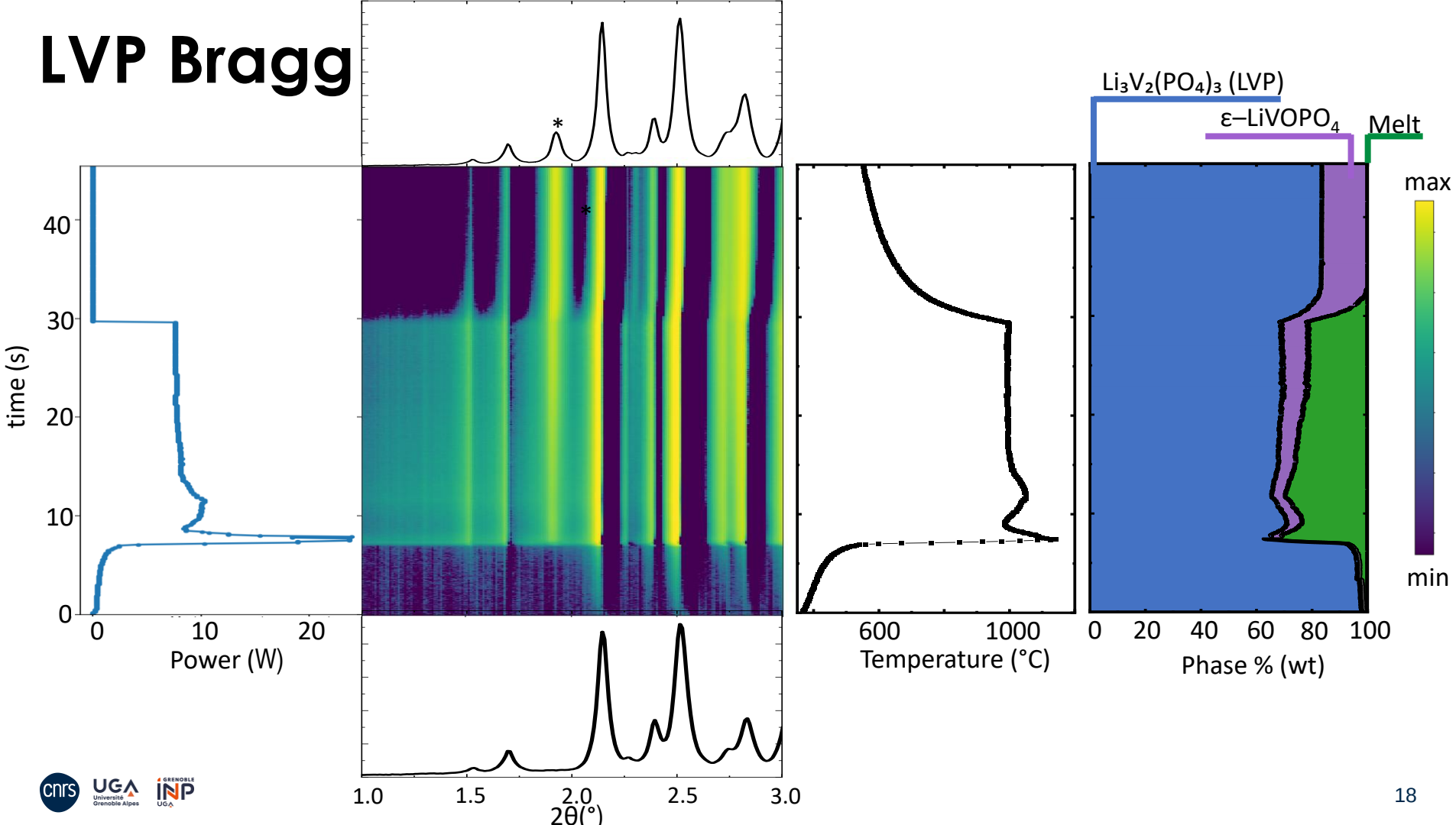
In-Situ FS Cell

Rapid total scattering scan: 50 ms/scan

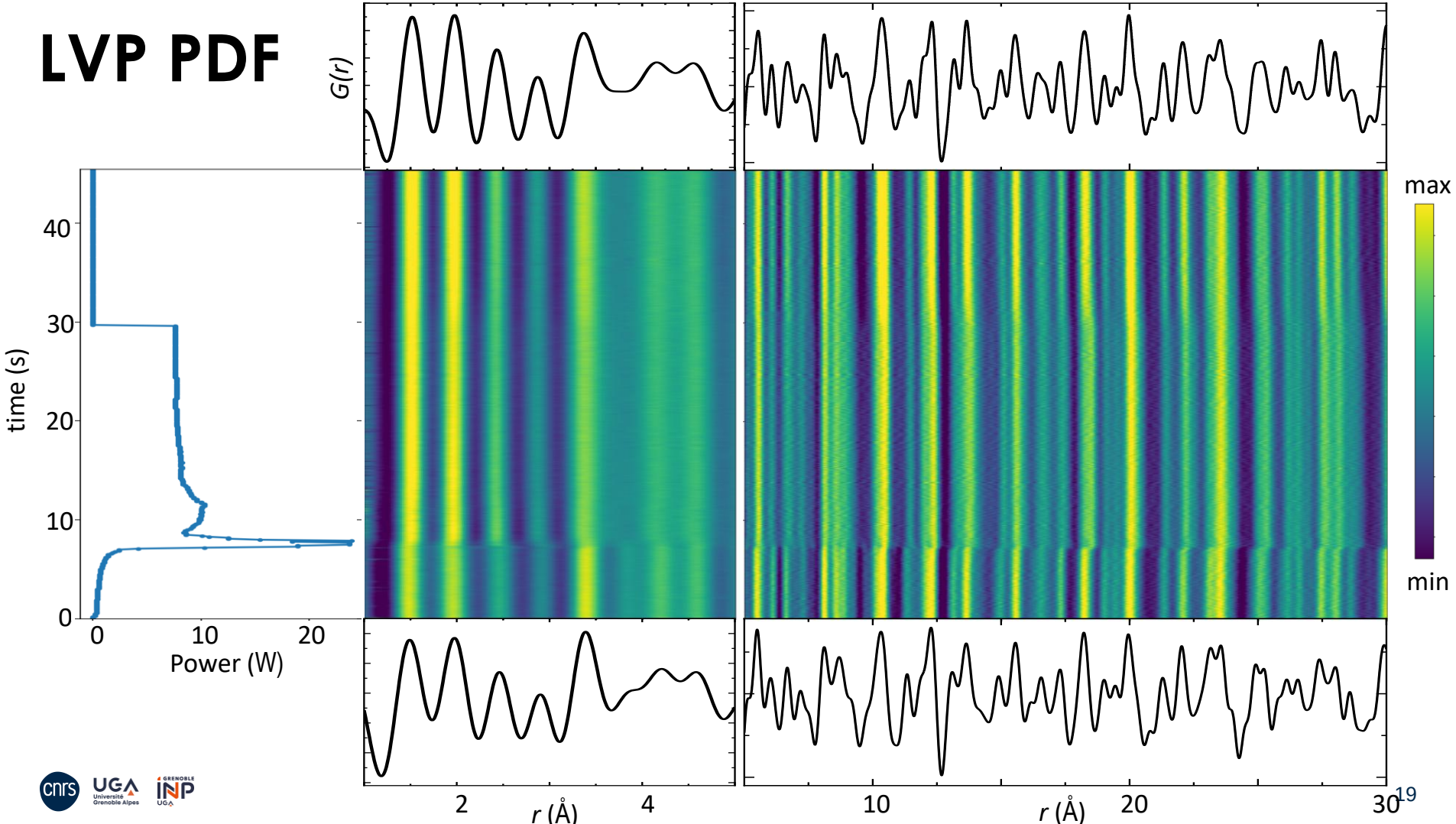




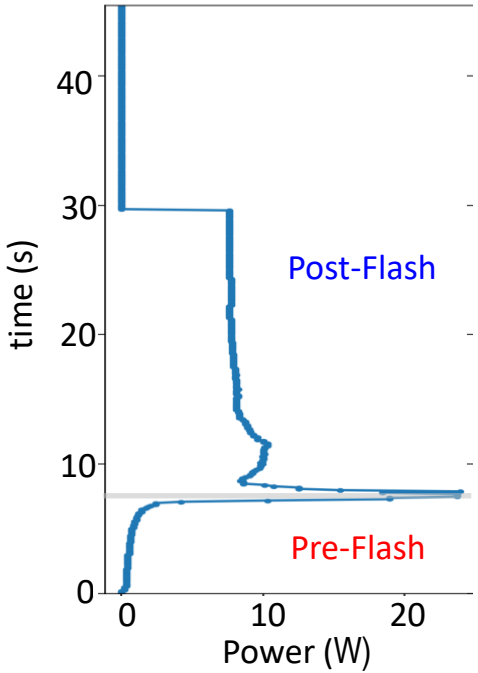
LVP Bragg

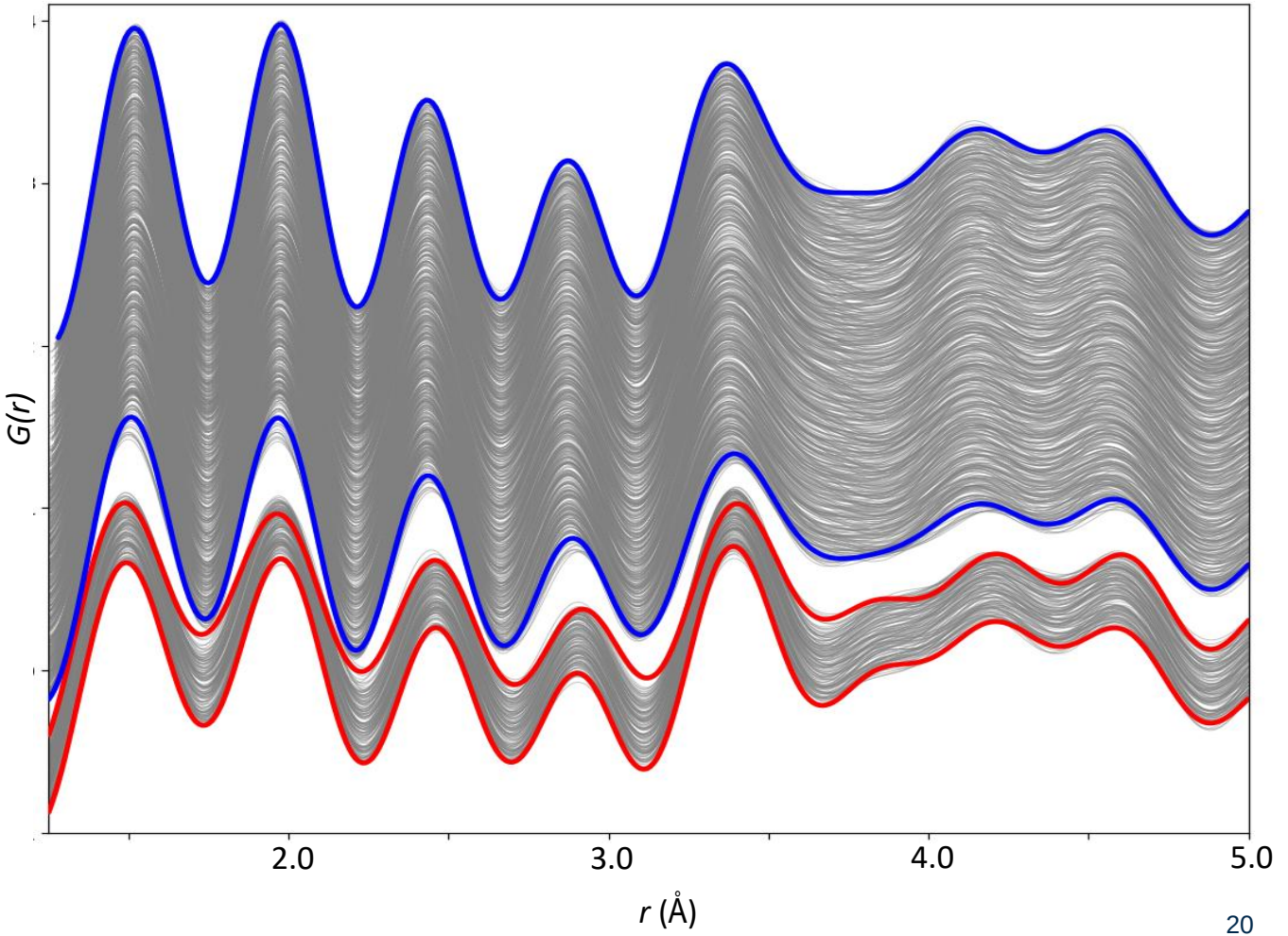

Li3V2(PO4)3 (LVP)
ε–LiVOPO4
Melt
max
min
time (s)
0
10
20
30
40
Power (W)
0
10
20
Temperature (°C)
600
1000
Phase % (wt)
0
20
40
60
80
100
2θ(°)
1.0
1.5
2.0
2.5
3.0
*
*

LVP PDF

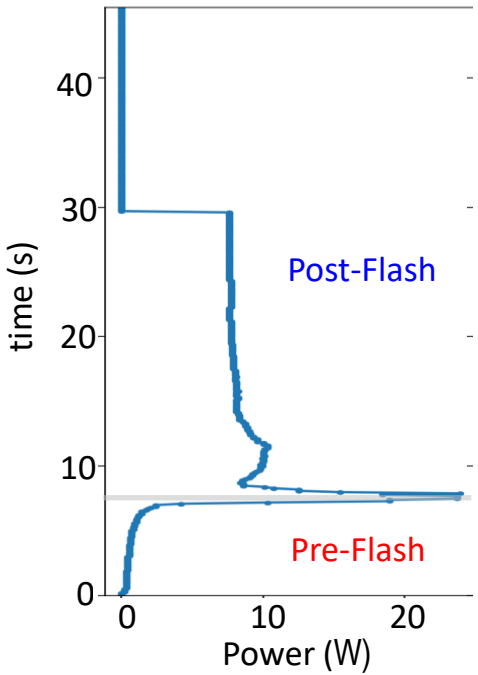


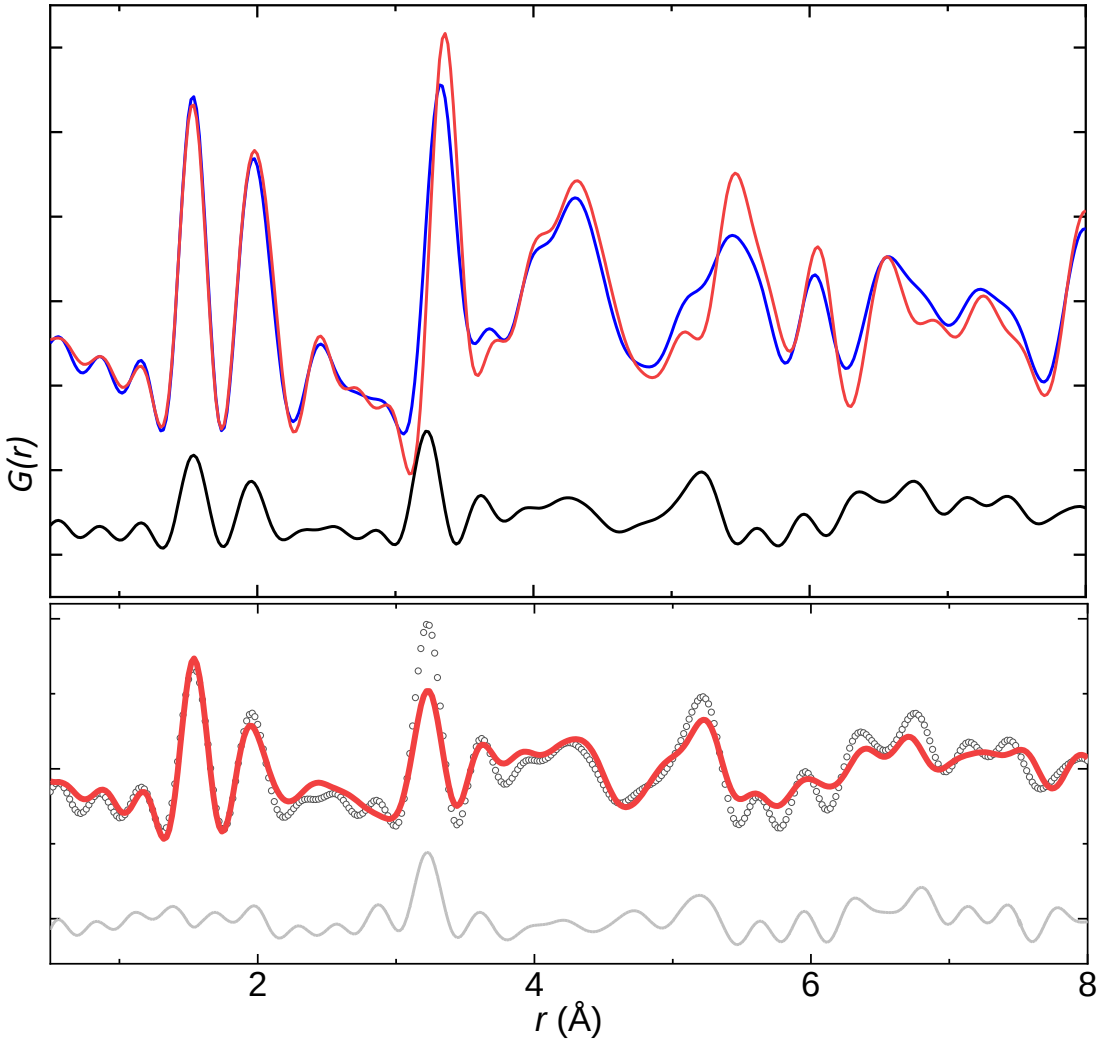
LVP PDF


time (s)
40
30
20
10
0
0
10
20
Power (W)
Post-Flash
Pre-Flash


G(r)
2.0
3.0
4.0
5.0
r (Å)

LVP PDF





Post-flash PDF (75% LVP + 25% LVOP

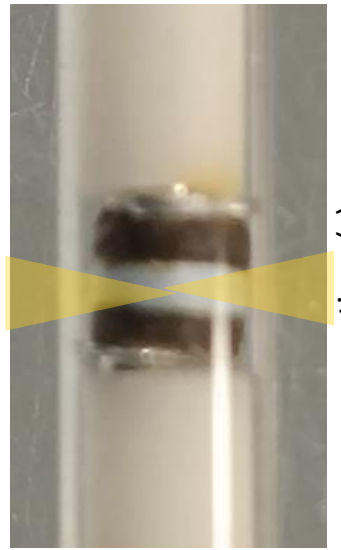
Pre-flash PDF (LVP reference)

Scaled Difference: LVOP contribution

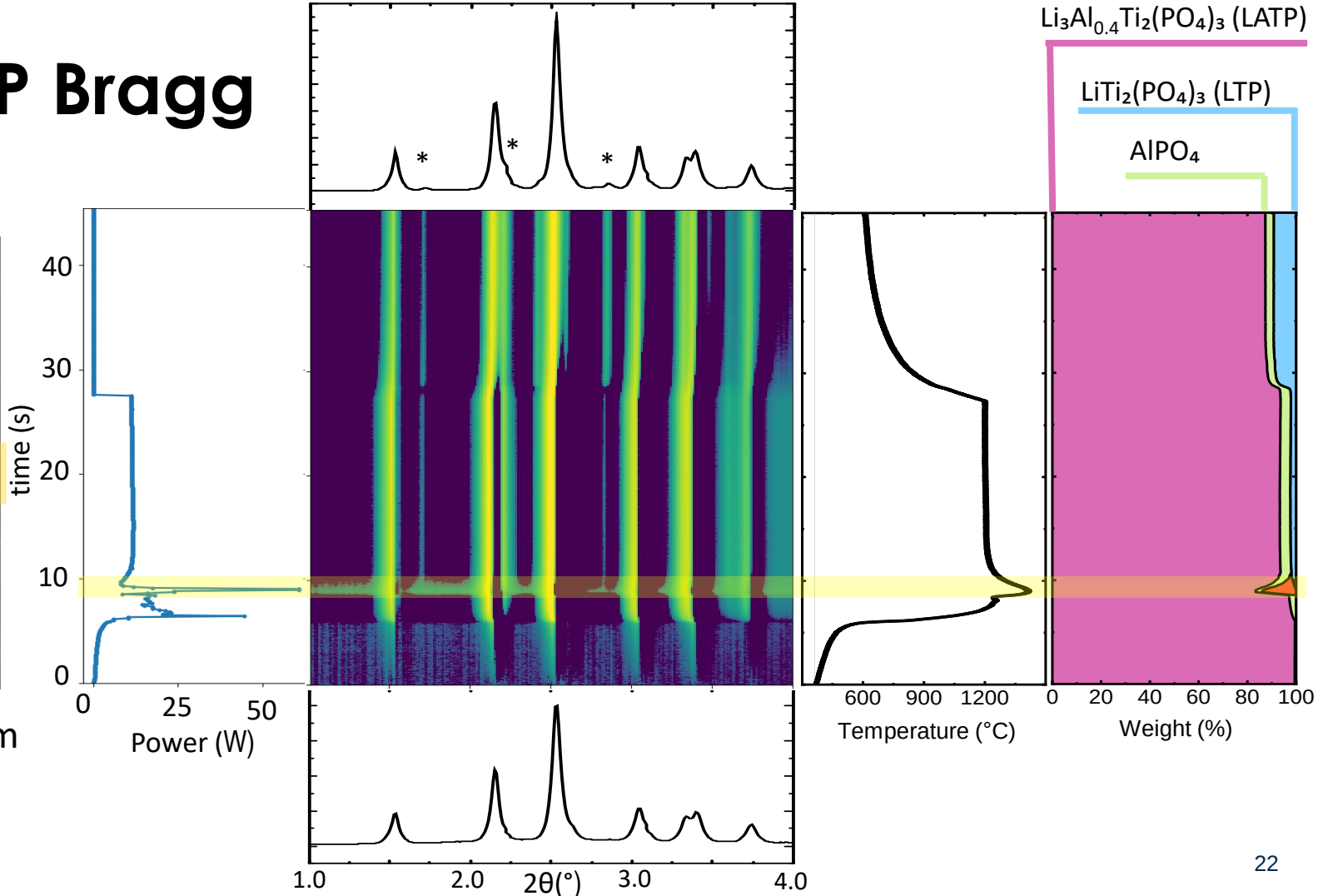
LVOP identified from PDF difference

Post-flash phase fractions are largely set at flash point.

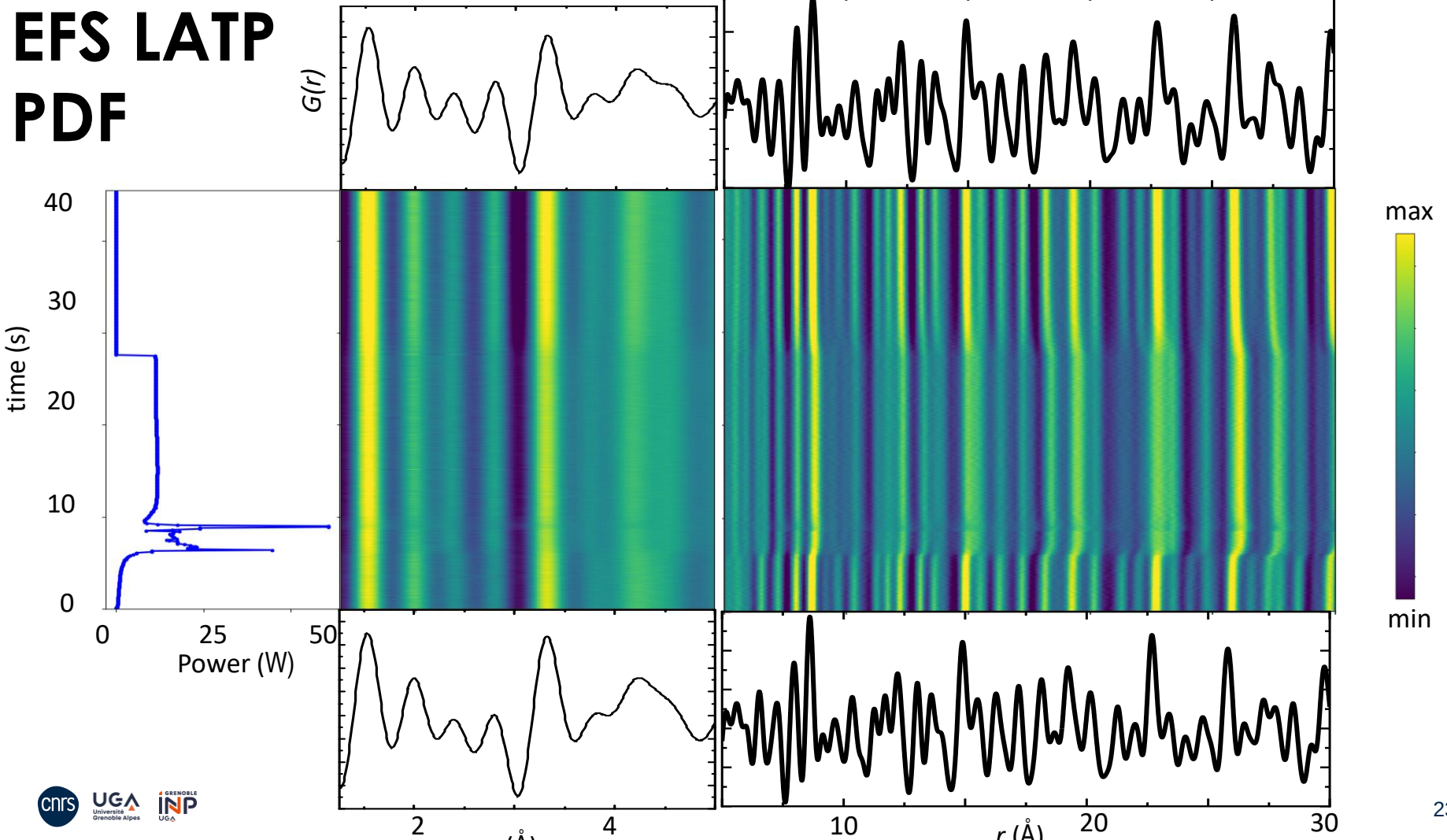
EFS LATP Bragg



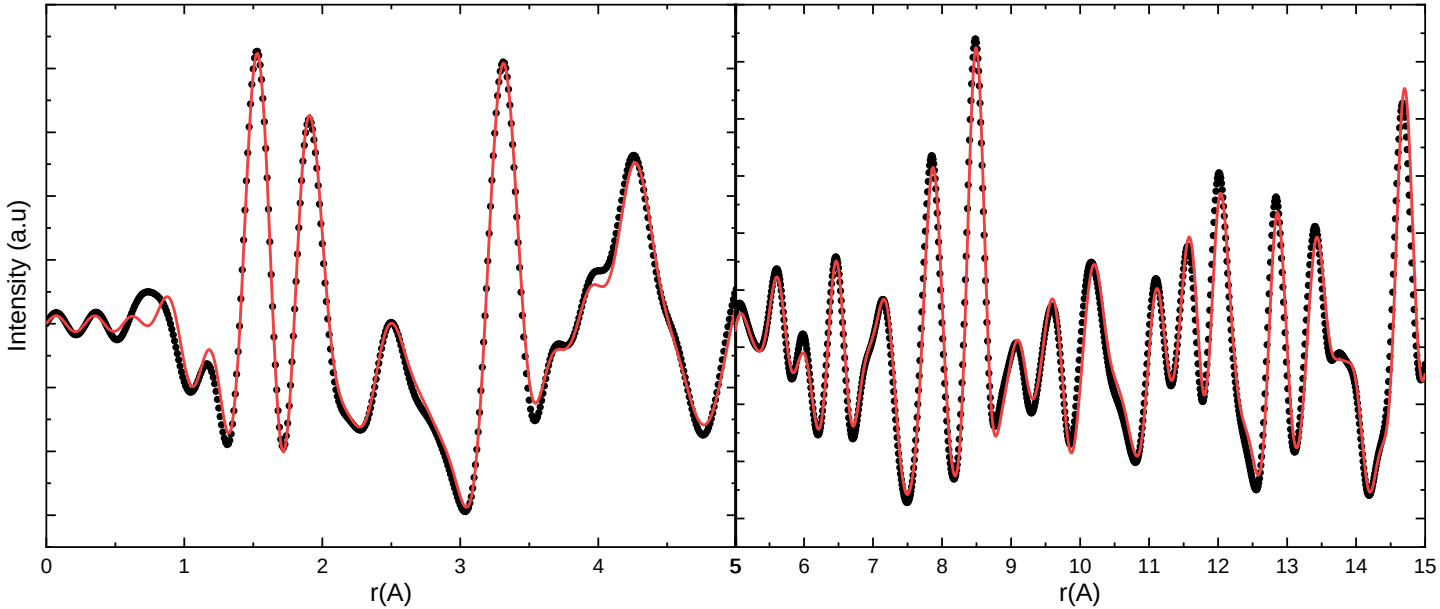
Multilayer system



EFS LATP PDF



EFS LATP



Post-flash PDF
(LATP + secondary phases)

Pre-flash PDF
(LATP reference)

Increased mechanical integrity and phase purity achieved by Electrochemical FS

Conclusion

In Conventional FS

- LVP decomposition is driven by Li^{+} volatility, leading to LVOP formation
- LATP decomposition arises from Ti^{4+} redox instability at high temperature, producing Ti^{4+}/Ti^{3+}-containing polymorphs

In Electrochemical FS

- Rapid sintering mitigates LATP–LVP interfacial reactivity in composites
- LATP can be densified under milder conditions in multilayers

In Future Work:

- Flash triggers instantaneous local structural changes.
- Future work should aim to control reaction outcome by tuning frequency and current parameters, not by current hold time.

Thank you for your attention

Contributors:

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