Supplementary information

Multi-scale characterization of submicronic NASICON-type solid electrolyte $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ degraded by spark plasma sintering

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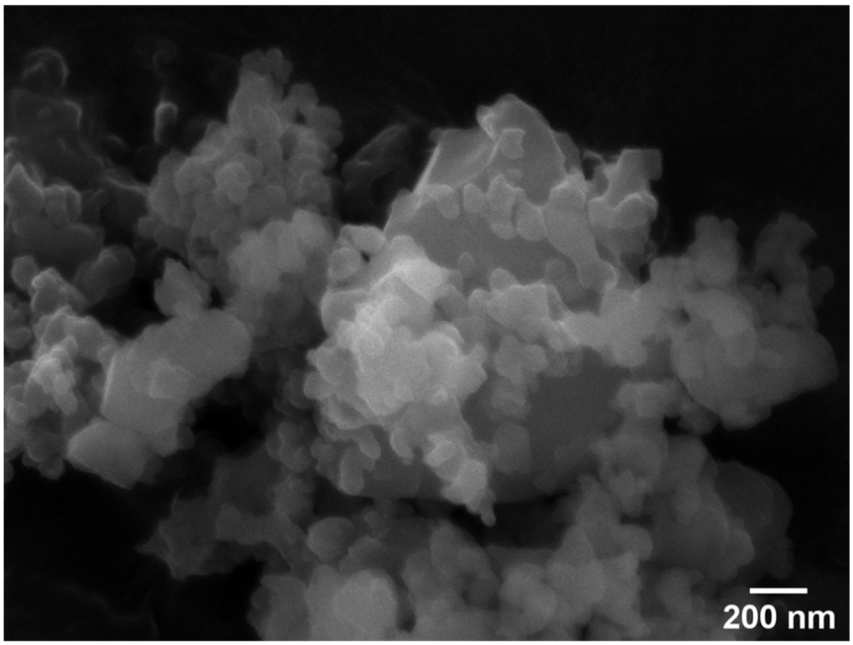
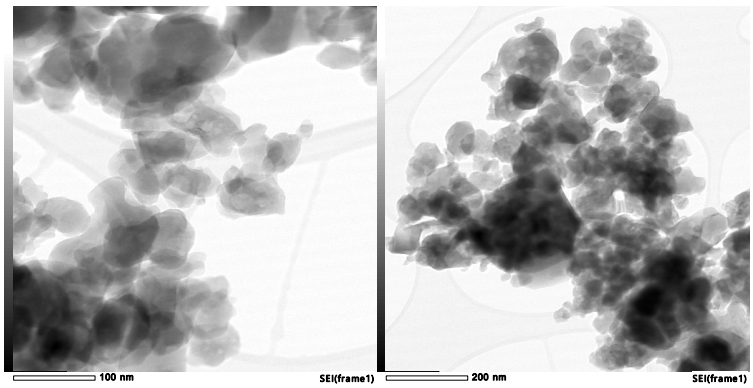
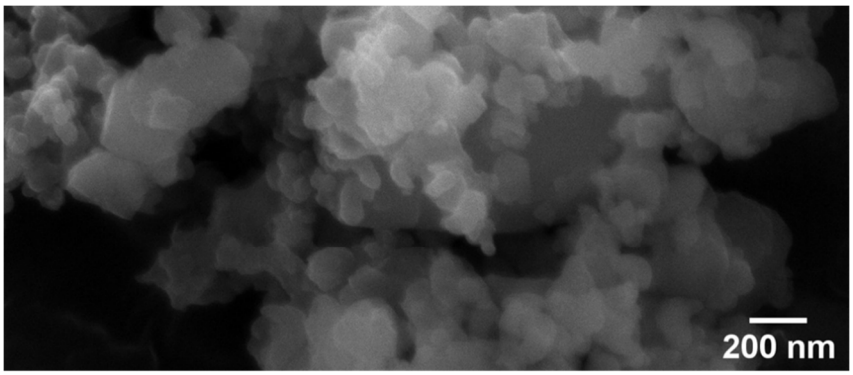
(a)







(b)

Element	*Atomic ratio*	*Nominal composition*	*Deviation (%)*

Figure S1: SEM and TEM images of primary submicronic particles of commercial LATP powder (a) ; results of ICP-OES chemical analyses performed for this LATP powder and their comparison with the expected nominal composition (b)

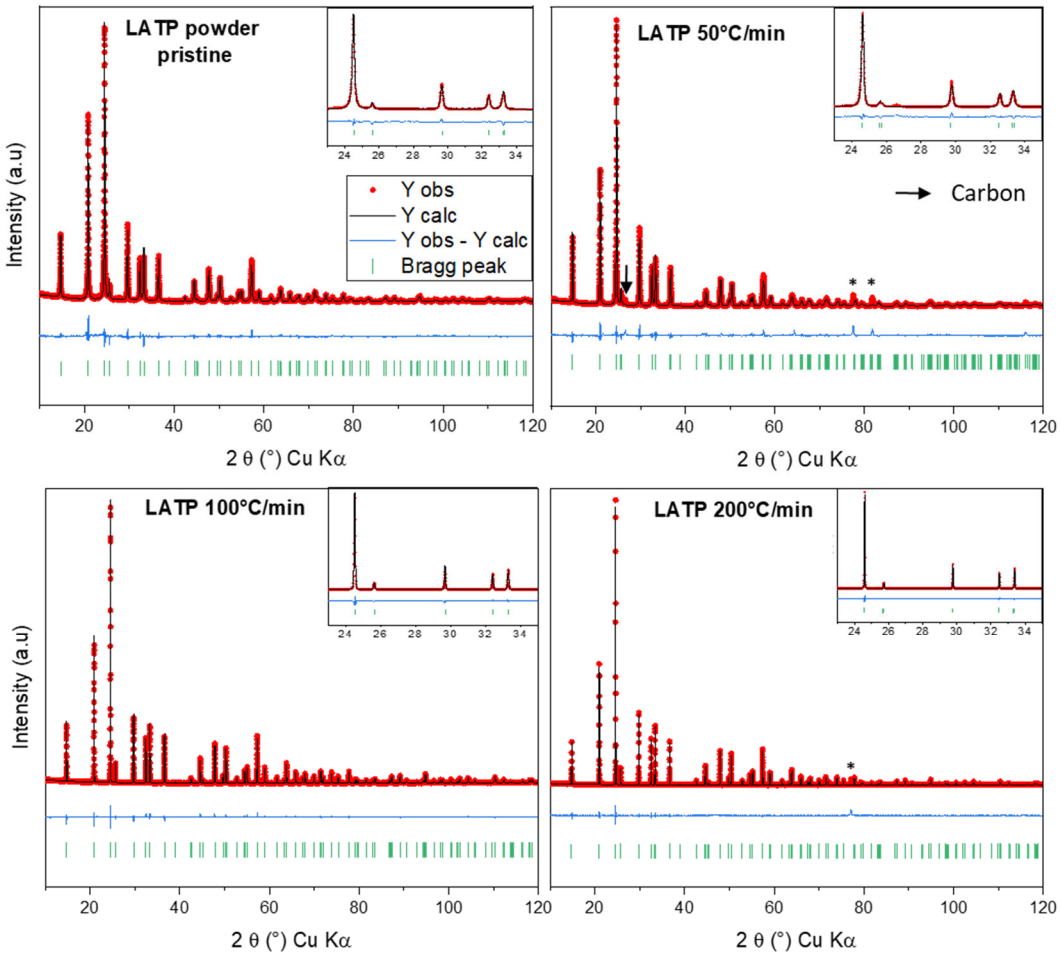


Figure S2: Rietveld refinements obtained for the pristine LATP powder and for the samples sintered by SPS at heating rates of 50°C/min, 100°C/min and 200°C/min

Table S1: Lattice parameters and cell volume determined by Rietveld refinement of XRD patterns

Sample	a (Å)	c (Å)	V (Å^3)
Pristine	8.505(2)	20.845(5)	*1305.8(6)*
LATP 50 °C/min	8.481(3)	20.884(9)	*1300 (1)*
LATP 73 °C/min	8.4987(2)	*20.8005(8)*	*1301.10(5)*
LATP 100 °C/min	8.5028(3)	20.8048(7)	*1302.61(8)*
LATP 200 °C/min	8.4988(4)	20.794(1)	*1300.7(1)*
LATP 300 °C/min	8.4996(2)	*20.7990(8)*	*1301.28(5)*
LATP CS 800°C, 5h	8.5006(2)	*20.8030(8)*	*1301.83(5)*

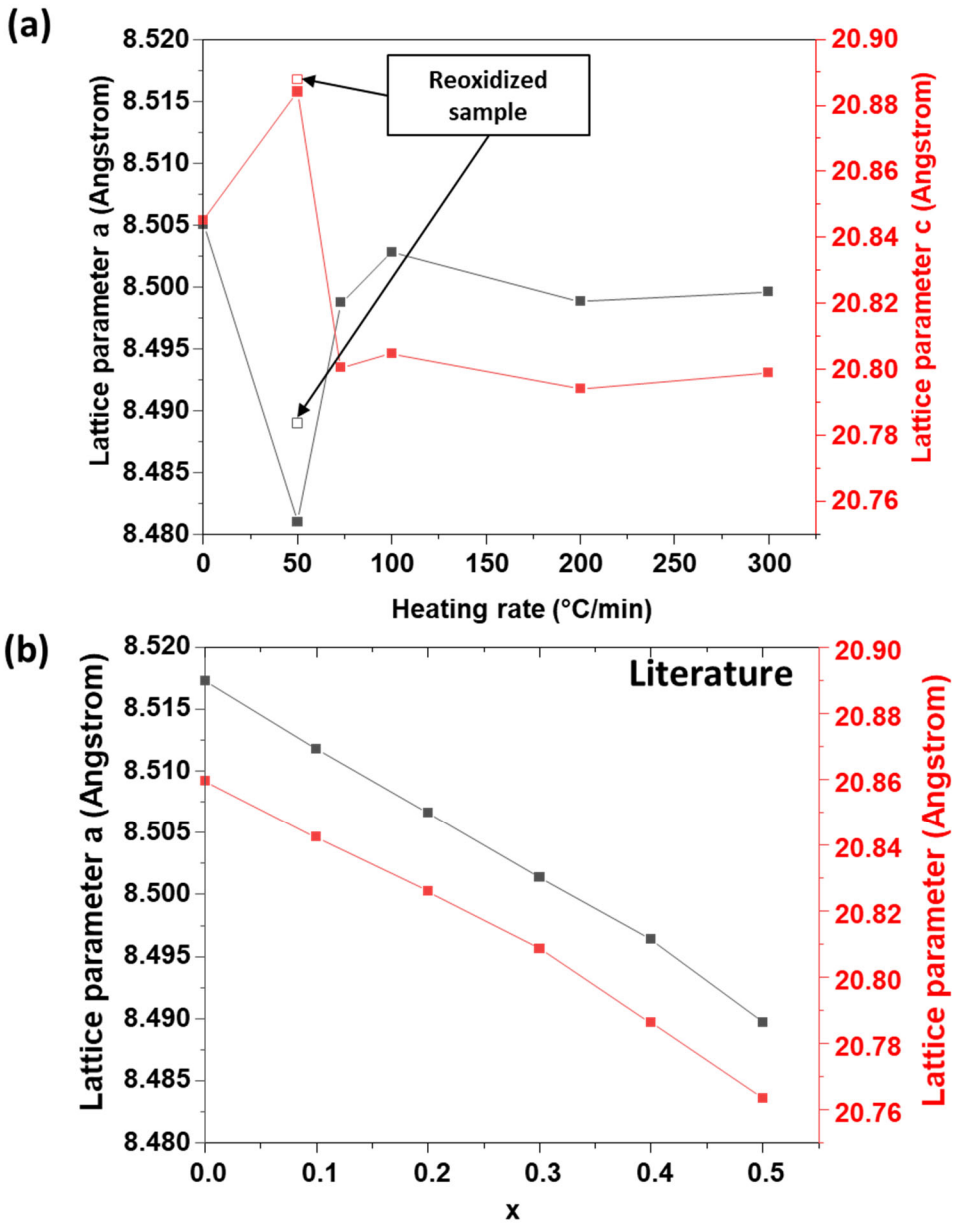


Figure S3: Evolution of the lattice parameters according to the heating rate applied during the SPS process (a) and lattice parameters evolution as function of the aluminium content inside the NASICON LATP structure, adapted from the reference [1](b). The lines are given to guide the eyes.

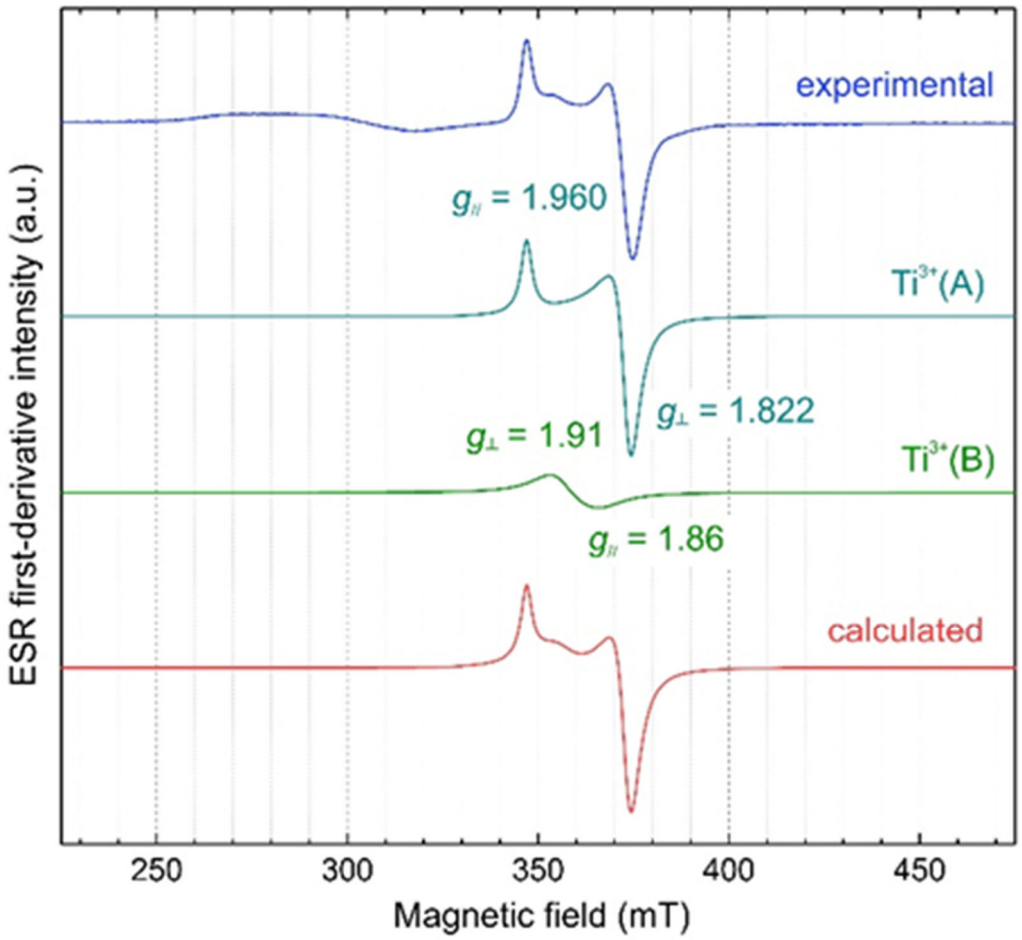


Figure S4 : Low temperature (30 K) X-band ESR powder spectra of sintered LATP (SPS 50°C/min) and simulated Ti^{3+} signals, and calculated spectrum (sum of Ti^{3+}(A) and Ti^{3+}(B) signals).

Table S2: Chemical shifts (δ), line widths (FWHM) and integrated intensities (II) of the different ^{27}Al MAS NMR signals observed for the spectra collected for pristine LATP and samples sintered by SPS using heating rates of 50°C/min and 200°C/min.

Composition	**AlO_6 (1)**			**AlO_6 (2)**			**AlO_4 ($AlPO_4$)**			**AlO_4/AlO_6 ratio**
Sample	**δ (ppm)**	**FWHM**	**II [%]**	**δ (ppm)**	**FWHM**	**II [%]**	**δ (ppm)**	**FWHM**	**II [%]**	
Pristine LATP	-14.93	3.85	**30.5**	-17.5	11.09	**24.42**	38.03	6.57	**45.08**	**0.82**
SPS 50°C/min	-14.85	3.68	**55.94**	-17.73	8.64	**29.46**	38.48	5.15	**14.6**	**0.17**
SPS 200°C/min	-15.89	3.63	**73.95**	-18.24	7.43	**18.07**	38.02	5.63	**7.98**	**0.08**

The chemical formula proposed for LATP were determined as explained hereafter.

If we assumed that Al content is shared such as the material contains {y mol $AlPO_4$ for 1 mol $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$}, the two Al-containing phases identified by XRD, and that we know in addition:

(i) From NMR, y/x
(ii) From ICP analyses that (x+y)/(2-x) = 0.3/1.7 or 2x + 1.7y = 0.6

It means that for:

- Pristine LATP: x = 0.18 and y = 0.14 and thus that the material is such as {0.14 mol $AlPO_4$ for $Li_{1.18}Al_{0.18}Ti_{1.82}(PO_4)_3$}
- SPS 50°C/min: x = 0.26 and y = 0.04 and thus that the material is such as {0.04 mol $AlPO_4$ for $Li_{1.26}Al_{0.26}Ti_{1.74}(PO_4)_3$}
- SPS 200°C/min: x = 0.281 and y = 0.022 and thus that the material is such as {0.02 mol $AlPO_4$ for $Li_{1.28}Al_{0.28}Ti_{1.72}(PO_4)_3$}

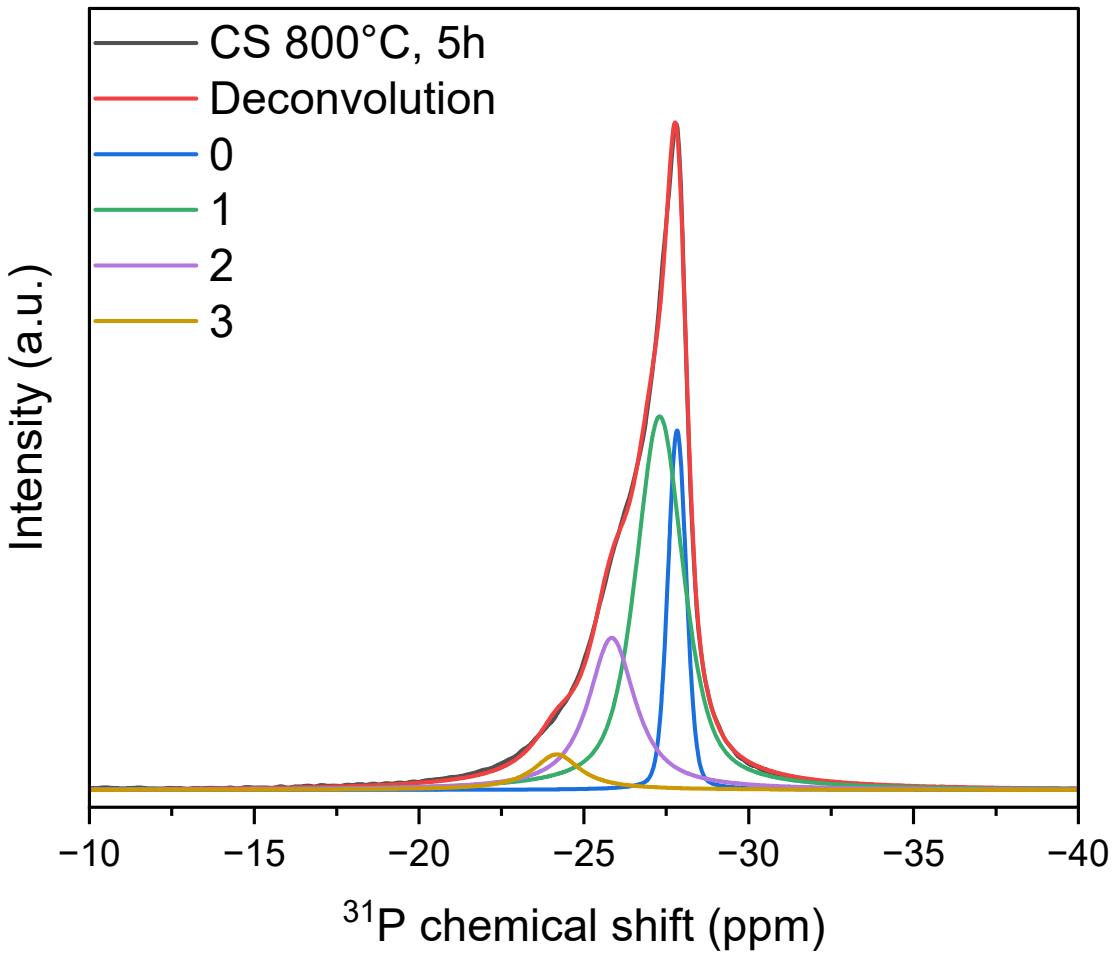


Figure S5: Fit of ^{31}P MAS NMR spectrum collected for the sample sintered conventionally at 800°C during 5h. It is given as an example to highlight the complexity of the fitting. The attribution of each contribution was done based on Arbi et al. work[2]. The blue, green, purple and orange contributions are associated to $P(OTi)_4$, $P(OTi)_3(OAl)_1$, $P(OTi)_2(OAl)_2$ and $P(OTi)_1(OAl)_3$ environments respectively. The one corresponding to $P(OAl)_4$ is obtained only for $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ compositions richer in Al (x > 0.3).

Table S3: Chemical shifts (δ), line widths (FWHM) and integrated intensities (II) of the different ^{7}Li MAS NMR signals observed for the spectra collected for pristine LATP, as well as samples sintered by SPS using heating rates of 50°C/min and 200°C/min.

Composition		**Li1 LATP**			**Li3 LATP**	
Sample	**δ (ppm)**	**FWHM**	**II [%]**	**δ (ppm)**	**FWHM**	**II [%]**
Pristine LATP	-1.04	0.47	**75.15**	- 0.62	2.16	**24.85**
SPS 50°C/min	-1.02	0.42	**54.5**	- 0.94	2.54	**45.5**
SPS 200°C/min	-1.27	0.22	**48.64**	-1.18	0.25	**51.36**

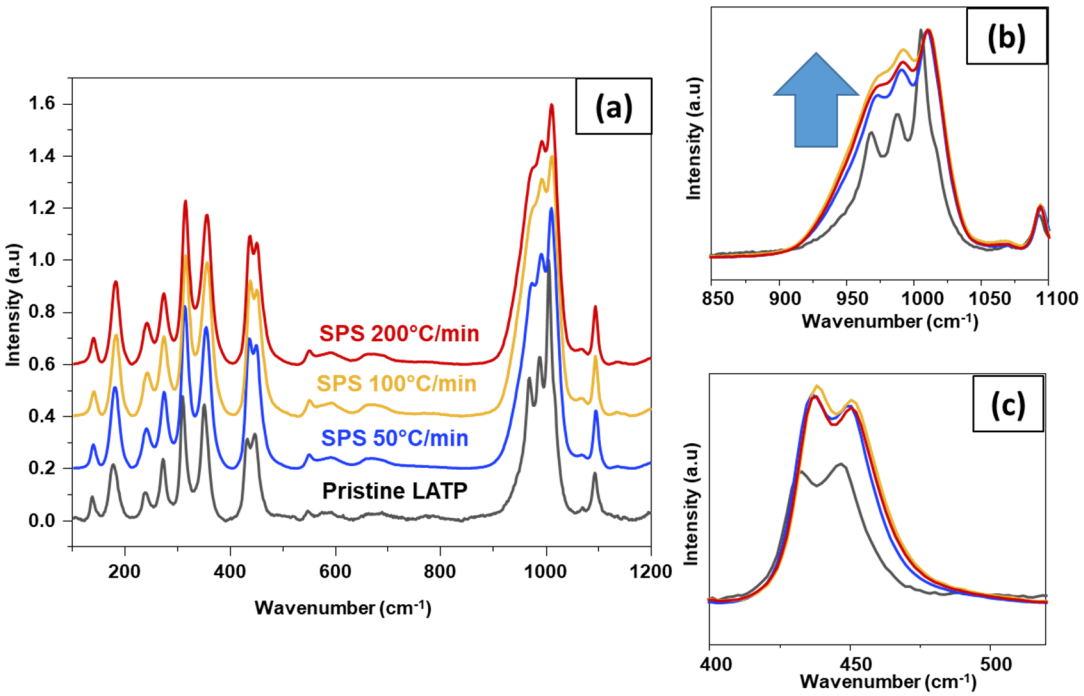


Figure S6 : Raman spectra of LATP pristine powder and samples sintered by SPS at heating rates of 50°C/min, 100°C/min and 200°C/min, obtained with a 532 nm laser in the range of 100 to 1200 cm^{-1} with an acquisition time of 15 s and 160 accumulations. (b) and (c) are enlargements of the spectra given in (a), but set at the same background reference level.

This figure shows the comparison of the Raman spectra of the different samples studied: pristine LATP, and samples sintered by SPS at heating rates between 50°C/min and 200°C/min. The Raman modes have for all the samples similar shapes and same positions between 100 cm^{-1} and 1200 cm^{-1}. However, compared to those collected for the pristine LATP powder the Raman modes of the sintered samples are broader, suggesting an increasing content of Al^{3+} inside the NASICON framework. Indeed, Cretin et al.[1] have shown that the partial substitution of Al for Ti inside the NASICON structure involves a general enlargement of the Raman spectra due to distortion of the octahedral ($(Ti/Al)O_6$) and tetrahedral (PO_4) sites. The higher the heating rate during the sintering by SPS, the higher are the relative intensities of the ν_1 bands at 969 and 992 cm^{-1} versus that of the ν_3 band at 1010 cm^{-1}. This evolution is linked to the increase of Al content inside the structure, which induces local disordering around the PO_4^{3-} anions. The peaks at 438 and 450 cm^{-1} can be ascribed to M-O symmetric bending motions (ν_2), whereas bands below 400 cm^{-1} arise from external modes[1–4].

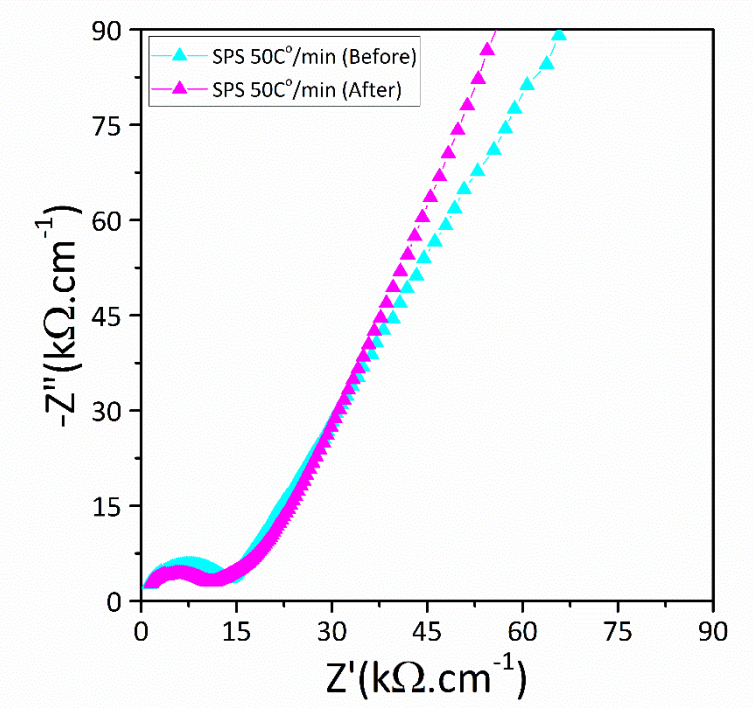


Figure S7: Impedance data collected at 25°C for LATP samples sintered by SPS at heating rate of 50°C/min before and after re-oxidation heat treatment (a). The complex impedance data shown here have been normalized regarding the shape factor of each sample for comparison purposes.

References

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