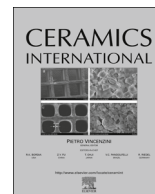




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Experimental and theoretical Raman study on the structure and microstructure of $\text{Li}_{0.30}\text{La}_{0.57}\text{TiO}_3$ electrolyte prepared by the sol-gel method in acetic medium

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ABSTRACT

In this report, we prepare LLTO ceramics by the sol-gel method in acetic medium. Raman spectroscopy showed the formation of lanthanum and titanium acetates precursors, which after calcination, lead to formation of the LLTO nanoparticles. Raman spectra were scanned directly over the LLTO pellets and the disappearance of impurities was observed during the microstructure evolution with increasing sintering temperature. X-ray diffraction characterization, including full pattern profile fitting refinements, showed no drastic changes in the unit cell parameters of the LLTO perovskite, but a large increase in the crystallite size domain was observed with increasing sintering temperature. Additionally, an interesting structural phase transition for the $\text{Li}_{0.30}\text{La}_{0.57}\text{TiO}_3$ perovskite structure was observed, from tetragonal $P4/mmm$ to distorted-cubic $Pm-3m$ spacegroup, for the highest sintering temperature ($T_s = 1300^\circ\text{C}$). Experimental and theoretical simulations of Raman spectroscopy confirmed the formation of a distorted-cubic phase and confocal Raman spectroscopy showed the presence of traces of impurities at the grain boundary region. In spite of the low total lithium conductivity observed, the electrochemical impedance spectroscopy analysis showed a remarkable increase in the lithium bulk conductivity for $T_s = 1300^\circ\text{C}$. This fact could be attributed to the structural phase transition from tetragonal to the cubic crystal system.

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1. Introduction

In the last years, the perovskite-type compound $\text{Li}_x\text{La}_{(2-x)/3}\text{TiO}_3$ (LLTO) has shown an excellent bulk ionic conductivity of up to 10^{-3} S/cm at room temperature [1] showing extensive potential applications in secondary solid state lithium batteries due to its high safety compared to liquid electrolytes [2,3]. LLTO crystalline structure has the perovskite ABO_3 general formula, basically constructed by TiO_6 octahedra, with Ti^{4+} occupying the B-sites and both $\text{Li}^+/\text{La}^{3+}$ ions occupying the A-sites in the perovskite structure. The vacancies in A-sites allow the lithium ions to move throughout the lattice showing good ionic conductivity over a wide range of compositions [4]. In addition, the LLTO microstructure also plays an important role on the ionic conductivity, thus the processing parameters such as sintering temperature affects drastically the lithium ion conduction [5,6]. On behalf of this,

the preparation methods are a crucial factor to enhance the lithium ionic conductivity. LLTO ceramics have been prepared generally using solid state reaction at high temperatures ($T \sim 1350^\circ\text{C}$) and long holding times ($t \sim 24\text{ h}$) leading to a serious loss of lithium and thus a declining of its ionic conductivity [7–9]. Therefore, the polymer precursor method or pulsed laser deposition method are usually performed to prepare LLTO ceramics [10–15]. The sol-gel derived methods require relatively low calcination temperature for the powder preparation, contributing to homogeneous mixing of the raw materials, highly stoichiometric composition and less lithium loss.

In this report, we prepare LLTO ceramics by the sol-gel method using titanium alkoxide precursor in acetic medium. The precursor formation and the crystal growth were studied using micro-Raman spectroscopy as an approach to understand its crystalline phase growing mechanism. Experimental and theoretical Raman simulations were performed to evidence local structural distortions which can not be detected using X-ray diffraction technique. Additionally, we also present for the first time a study on the sintering process using confocal Raman imaging technique in

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order to evaluate, simultaneously, the structure, microstructure and chemical composition at the LLTO grain boundary interface. Raman spectroscopy shows higher accuracy in the detection of lithium phase impurities in comparison with conventional X-ray powder diffraction. Electrochemical impedance spectroscopy was performed in order to study the lithium conduction mechanism and its correlation with structural and microstructural trends observed in Raman and Rietveld analyses.

2. Materials and methods

Lanthanum oxide (La_2O_3) and lithium carbonate (Li_2CO_3) were dissolved in 5 mL of acetic acid and 0.5 mL of deionized water under stirring at $\sim 70^\circ\text{C}$ until a white homogeneous solution was formed. The precursor solution (LL-ac) was prepared using a Li:La ratio of $X: (2-X)/3$ with $X=0.30$ and titanium isopropoxide (Ti-TIP) was added afterward in a Ti: La ratio of $1: (2-X)/3$. The white solution turned into a transparent solution and was kept stirring and heated at 100°C during 7 h to form LLTO-100(t) with t being the time of heating. LLTO-100(7) was then heated at 600, 700, 800 and 900°C during 1 h in static air to obtain LLTO-T with T being the temperature of heating. LLTO-900 were pressed into pellets and sintered at $T_s = 1000\text{--}1300^\circ\text{C}$ during 1 h in static air to obtain the sintered samples named as LLTO-900- T_s with T_s being the sintering temperature.

The LLTO-100(t) sol-gel precursors were studied in glass vials during the gelification process by Raman spectroscopy using DeltaNu Advance 532 Spectrometer with a 532 nm laser wavelength and 30 mW laser power. Every hour, a set of 30 spectra of 5 s integration time were averaged to monitor the gelification at different times ($t=1\text{--}7$ h). LLTO-T nanoparticles and LLTO-900- T_s sintered pellets were studied by micro-Raman spectroscopy using WITec Alpha 300-RA with a 532 nm laser wavelength and 30 mW laser power. In this case, a set of 20 spectra of 0.2 s integration time were averaged for each sample.

Raman theoretical spectra simulations were obtained using the VASP code [16–19] to calculate vibrational properties using DFPT (Density Functional Perturbation Theory) and a post-processing

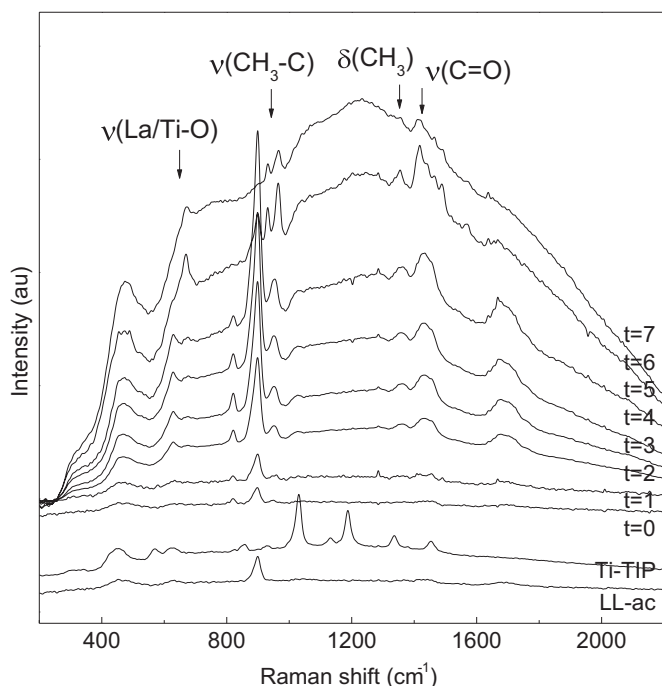


Fig. 1. Raman spectra for LL-ac, Ti-TIP and LLTO-100(t) with $t=0\text{--}7$ h.

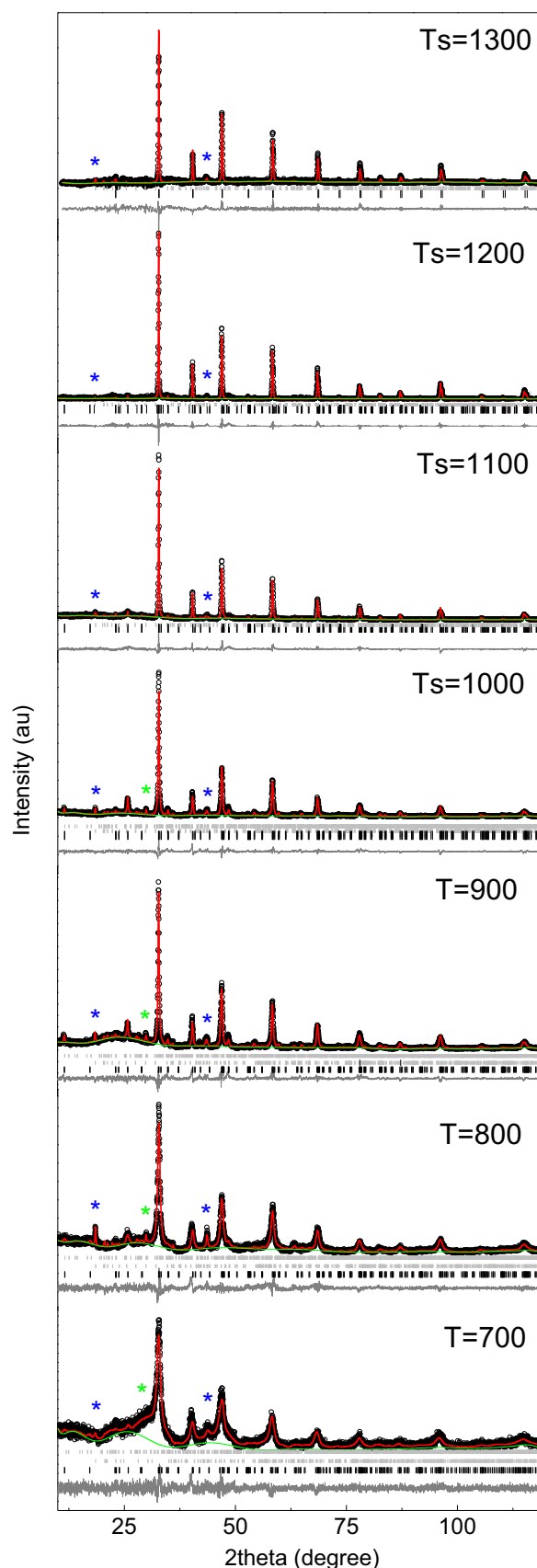


Fig. 2. XRPD patterns and Rietveld analysis for LLTO-T with $T=700, 800, 900$ and LLTO-900- T_s with $T_s=1000, 1100, 1200, 1300$. Li_2TiO_3 and $\text{La}_2\text{Ti}_2\text{O}_7$ impurities are marked with blue and green asterisks, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

tool for Raman activity [20,21]. The structural models for the calculations were constructed based on the Rietveld refinement cell parameters results and then supercells were constructed to achieve the composition. The dimensions of the supercells as a repetition of the ideal cubic perovskite cell (with $a_p \sim 3.86$ Å) were $3 \times 3 \times 1$ for the cubic and $3 \times 2 \times 2$ for the tetragonal. In both cases A-site ion defect was considered and the simulated compositions for each case were $\text{La}_{0.56}\text{Li}_{0.33}\text{TiO}_3$ for cubic (44 atoms) and $\text{La}_{0.58}\text{Li}_{0.33}\text{TiO}_3$ for tetragonal (59 atoms). The PBE [22] generalized gradient approximation (GGA) functional with Dudarev approach (GGA+U) has been used, and the projector-augmented wave method (PAW) [23,24] has been employed to treat the atomic cores. A single parameter $U_{\text{eff}} = U - J$ was employed for Ti 3d level electrons with a value of $U_{\text{eff}} = 1.2$. The precision setting for the VASP calculations was set to the one that corresponds to a global plane-wave energy cutoff of 400 eV and a k-point grid of $2 \times 2 \times 4$ and $1 \times 2 \times 2$ has been employed for cubic and tetragonal structures, respectively.

Structural analysis was performed by X-ray powder diffraction using a Rigaku Ultima IV, $\text{CuK}\alpha$ radiation in the 2θ range = 10 – 120° and a step of 0.02° with integration time of 5 s. Rietveld refinement was performed using GSAS-EXPGUI software package [25,26]. LLTO-900-Ts sintered pellets were coated with a silver paste on both sides and studied by electrochemical impedance spectroscopy (EIS) using AC impedance spectroscopy in the 0.1 Hz–1 MHz frequency regime using a Gamry Reference 3000 impedance analyzer, at room temperature. Data processing was performed using Echem Analyst software.

3. Results and discussion

3.1. LLTO sol-gel precursor formation

Raman spectra of LL-ac solution precursors showed the presence of acetic acid typical vibrational modes as it is observed in Fig. 1. Two broad peaks at ~ 440 and 620 cm^{-1} were observed and ascribed to C-O-H twisting and $\delta(\text{O}=\text{C}-\text{OH})$ bending modes, respectively. A sharp peak located at $\sim 900\text{ cm}^{-1}$ was attributed to the symmetric stretching of $\text{CH}_3\text{-COH}$ group. Two broad peaks were also observed at ~ 1420 and 1680 cm^{-1} , attributed to the asymmetric deformation of methyl group and carbonyl stretching, respectively [27]. Ti-TIP showed the presence of broad peaks at ~ 320 , 430, 590 and 850 cm^{-1} , attributed to $\delta(\text{Ti-O}_4)$, $\nu(\text{Ti-O}_4)$, $\delta(\text{O-C-CH}_3)$ and $\nu_s(\text{CH}_3\text{-C-CH}_3)$ vibrational modes, respectively. Other sharp peaks with higher intensity were observed at ~ 1030 , 1190, 1340 and 1480 cm^{-1} and ascribed to $\nu_{\text{as}}(\text{CH}_3\text{-C-CH}_3)$, $\nu_{\text{as}}(\text{O-C-CH}_3)$, $\delta(\text{C-C-H})$ and $\delta(\text{H-C-CH}_3)$ vibrational modes, respectively.

Raman analysis performed on LLTO-100(t) samples, performed immediately after the addition of Ti-TIP into the LL-ac solutions at 100°C , showed the presence of sharp peaks at ~ 822 and 1396 cm^{-1} probably attributed to $\nu_s(\text{CH}_3\text{-C-CH}_3)$ and $\delta(\text{C-O-H})$ vibrational modes of isopropyl alcohol (IPA), respectively. At $t=2$, sharp peaks at ~ 899 and 1700 cm^{-1} were observed, probably ascribed to $\nu_s(\text{CH}_3\text{-C-OR})$ and $\nu_s(\text{C=O})$ modes of isopropyl acetate, as it was already reported for the analogous butyl acetate ester [28]. After the gel was formed ($t=7$), sharp peaks were observed at ~ 631 , 930–964, 1360 and 1429 cm^{-1} and were assigned to $\nu_s(\text{La/Ti-O})$, $\nu_s(\text{CH}_3\text{-C})$, $\delta(\text{CH}_3)$ and $\nu_s(\text{C=O})$ modes of lanthanide and titanium acetate chelates, respectively [29]. X-ray diffraction patterns for the LLTO-100(5) dry gel precursor showed the presence of typical ($h\ k\ l$) reflections ascribed to lanthanum acetate $\text{La}(\text{CH}_3\text{CO}_2)_3$ and other minor intensity peaks that could be associated with titanium acetate complexes, in agreement with Raman analysis discussed previously.

3.2. LLTO crystalline phase formation

The formation of the $\text{Li}_x\text{La}_{(2-x)/3}\text{TiO}_3$ perovskite nanoparticles was observed after calcination of the La/Ti acetate precursor above $T=700^\circ\text{C}$, as shown in Fig. 2. Mean crystalline domain size (D), estimated by the Scherrer equation [30], showed a typical increase for LLTO-T samples with increasing calcination temperature, as shown in Table 1. D values obtained for LLTO-T were $D \sim 12$, 19 and 43 nm for $T=700$, 800 and 900, respectively.

Rietveld analysis confirmed the formation of the $\text{Li}_{0.30}\text{La}_{0.57}\text{TiO}_3$ crystalline phase, best fitted in the tetragonal $P4/mmm$ space group. Minor impurities were observed and ascribed to $\text{La}_2\text{Ti}_2\text{O}_7$ and Li_2TiO_3 , best fitted in the monoclinic $P21$ and $C2/c$ space group, respectively. The presence of these impurities is reduced with increasing calcination temperature, stabilizing the $\text{Li}_{0.30}\text{La}_{0.57}\text{TiO}_3$ phase at $T=900^\circ\text{C}$. A slight compression of the unit cell c parameter is observed with increasing annealing temperature, as summarized in Table 1. The lanthanum occupancy showed the formation of typical La-rich and La-poor planes in the tetragonal structure. Additionally, a slight enlargement for the mean Ti-O bonds was observed with increasing calcination temperature. This average enlargement could be ascribed to the enhancement in the interaction between oxygen (O^{2-}) and lithium (Li^+) ions, thus reducing the Ti-O interaction, as reported by Chen et al. [31].

Raman spectra for LLTO-T with $T=700$ – 900 (Fig. 3), showed the presence of peaks located at ~ 148 , 245, 320, 530, 560 and 878 cm^{-1} , which can be attributed to the $\text{Li}_{0.30}\text{La}_{0.57}\text{TiO}_3$ vibrational modes in the tetragonal $P4/mmm$ structure. These experimental values are in good agreement with and those calculated shown in Table 2 and also with those observed experimentally in a

Table 1

Rietveld analysis and mean crystallite size (D) estimation using Scherrer equation for LLTO-T with $T(^{\circ}\text{C})=700$, 800, 900 and LLTO-900-Ts with $T_s=1000$, 1100, 1200, 1300.

LLTO-T	$T=700$	$T=800$	$T=900$	$T_s=1000$	$T_s=1100$	$T_s=1200$	$T_s=1300$
Spacegroup	$P4/mmm$	$P4/mmm$	$P4/mmm$	$P4/mmm$	$P4/mmm$	$P4/mmm$	$Pm-3m$
$a=b$ (Å)	3.888(2)	3.8777(7)	3.8738(3)	3.8802(2)	3.8783(2)	3.8761(2)	3.8716(2)
c (Å)	15.65(2)	15.571(6)	15.559(2)	15.491(2)	15.491(2)	15.4808(12)	3.8716(2)
$d(\text{Ti-O})$ (Å)	1.945(25)	1.929(23)	1.968(15)	1.994(8)	2.172(4)	1.961(25)	1.93581(9)
La1 (Occup)	0.49(3)	0.33(3)	0.31(2)	0.295(12)	0.327(10)	0.41(3)	0.390(5)
La2 (Occup)	0.51(3)	0.44(4)	0.29(2)	0.296(14)	0.419(10)	0.39(3)	–
La3 (Occup)	0.70(3)	0.633(14)	0.583(7)	0.613(8)	0.503(6)	0.520(11)	–
L_x	62.8(3)	40.0(15)	17.2(6)	12.2(2)	8.07(13)	5.0(5)	0.7(2)
D (nm)	11.82(21)	18.55(24)	43.14(5)	60.82(4)	91.95(6)	> 100	> > 100
χ^2	0.9633(47v)	1.341(47v)	1.431(45v)	1.671(46v)	1.805(40v)	2.019(41v)	0.996(32v)

Mean crystallite diameter estimations (D) were performed using the lorentzian component (L_x) from the Rietveld analysis based in the equation $D=18,000K/\pi L_x$ [26]. The Scherrer constant $K=0.94$ and λ is the wavelength (0.15418 nm). D values for $T_s=1200$ and 1300 are high enough above the application limit of the Scherrer equation and only the lower limit is given.

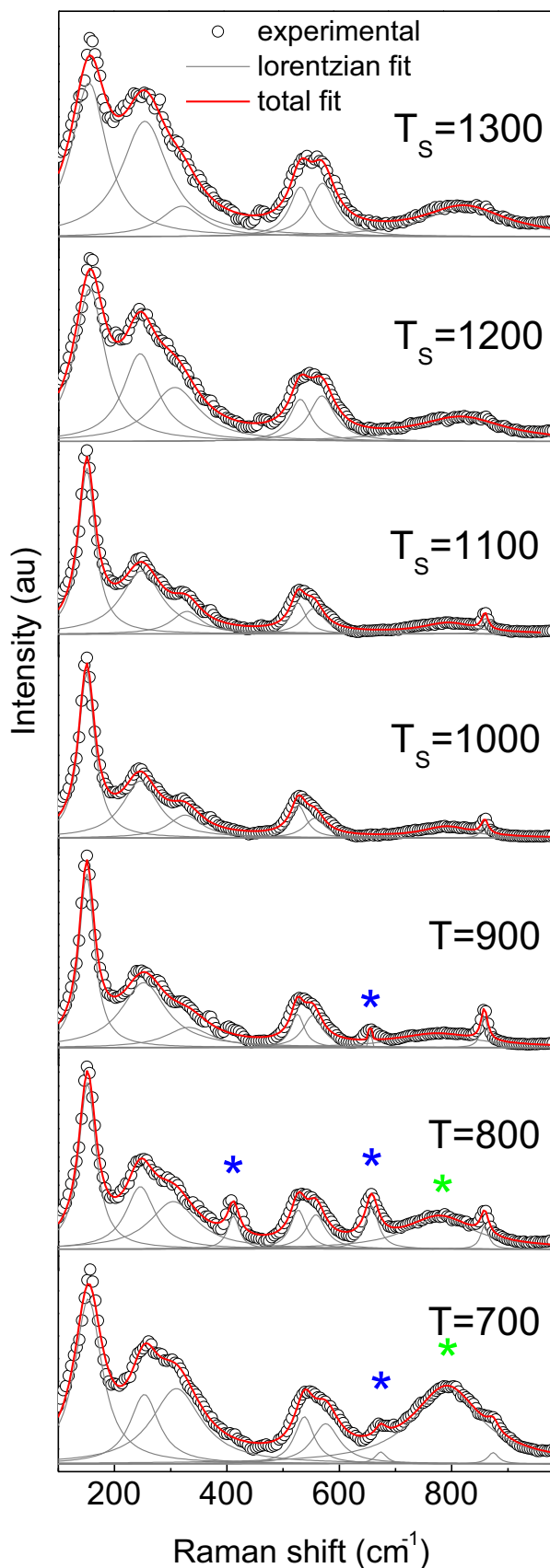


Fig. 3. Experimental Raman spectra and Lorentzian fittings for LLTO-T with $T=700$, 800, 900 and LLTO-900-Ts with $T_s=1000$, 1100, 1200, 1300. Li_2TiO_3 and $\text{La}_2\text{Ti}_2\text{O}_7$ impurities are marked with blue and green asterisks, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2

Theoretical Raman shift (ω) and vibrational modes assignment for $\text{Li}_{0.3}\text{La}_{0.57}\text{TiO}_3$ in distorted-cubic and tetragonal supercell structures.

$\omega_{\text{d-cubic}}$ (cm^{-1})	$\omega_{\text{tetragonal}}$ (cm^{-1})	Assignment
168	142	Ti displacement (x-y)
254	252	Ti-O ₆ tilt (x-y)
320	324	Ti displacement (z)
422	429	Ti-O ₆ tilt (z)
549	543	Ti-O ₆ tilt (x-y)
557	560	Ti-O ₆ tilt (z)
853	844	Ti-O, Li-O symmetric stretching (x-y)

Theoretical Raman shift were calculated using GGA+U method for the supercell structures shown in Fig. 7.

previous report [32]. The high cross section of phonons located at $\sim 148 \text{ cm}^{-1}$ are associated to the Ti displacements in the x-y plane constituting the E_g mode. Those found at ~ 245 and $\sim 320 \text{ cm}^{-1}$ are associated to the A-site cation displacement corresponding to E'_g and A_{1g} modes, respectively. The phonons in high-frequency regions contribute to oxygen movement; the peak at $\sim 420 \text{ cm}^{-1}$ corresponds to the O-Ti-O displacement along the z-axis of the A_{1g} mode and the peaks at 531 and 560 cm^{-1} are analogous to the E_g and A_{1g} modes [33], named E'_g and A'_{1g} , respectively. In the present report, the low intensity peak at $\sim 878 \text{ cm}^{-1}$ was associated with the symmetric stretching of both Ti-O and Li-O bonds along the x-y plane, as shown in Table 2.

Raman shift frequency is plotted in Fig. 4a, showing its dependence with calcination temperature. The position of most of the Raman peaks showed almost no shifting, with the exception of the A'_{1g} mode located at $\sim 560 \text{ cm}^{-1}$, which showed a slight red shift with increasing calcination temperature. Additionally, a sharpening of the peaks was observed with increasing calcination temperature, evidenced by the decrease in the linewidth (Γ), as shown in Fig. 4b. The decreasing of the Raman linewidth (Γ) is usually associated to the increase of the crystallite size (D). The broad peaks usually observed for small nanoparticles are mostly attributed to the phonons confinement effect. In our case, the Raman linewidth (Γ) associated to the E_g mode showed a linear dependence with $D^{-3/2}$ for LLTO-T with $T=700$, 800 and 900 (Fig. 4b-inset), in agreement with the tridimensional phonon confinement model [34]. On the other hand, the intensity of the Raman peak located at $\sim 320 \text{ cm}^{-1}$, ascribed to the A_{1g} mode, declines with increasing calcination temperature. This behavior could be attributed to the lithium enrichment of the LLTO phase, accompanied with a consequently decrease in the impurity content of the Li_2TiO_3 phase. It is important to mention that the decrease in the intensity of the peak located at $\sim 320 \text{ cm}^{-1}$ could also be associated to a change in the symmetry environment of Ti atoms in quenched samples [33].

3.3. LLTO sintering

X-ray diffraction patterns for LLTO-900- T_s showed the progressive disappearance of both $\text{La}_2\text{Ti}_2\text{O}_7$ and Li_2TiO_3 impurities with increasing sintering temperature (T_s). Rietveld refinement results (Table 1) showed a slight compression in the unit cell parameters and a reduction in the Ti-O bonds mean distance with increasing T_s , probably related to the beginning of lithium loss at high temperatures ($T > 1200^\circ\text{C}$). The lanthanum occupancy in all positions (La1, La2 and La3) tends to equalize with increasing T_s , in agreement with the increase of the crystalline symmetry. The mean crystallite domain size (D) showed a drastic increase with increasing T_s , evidencing the sintering process. Rietveld refinements suggested a crystal phase transition for $T_s=1300$, from the

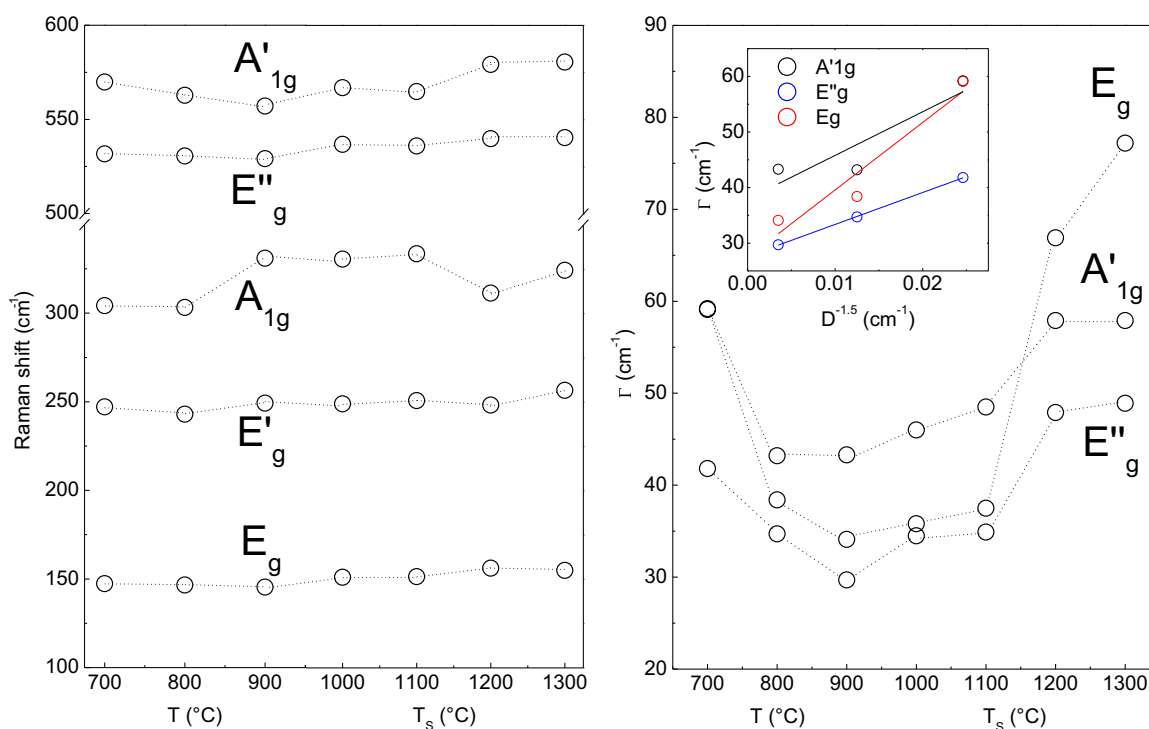


Fig. 4. Raman shift (a) and linewidth (b) versus annealing temperature for LLTO-T with $T=700, 800, 900$ and LLTO-900- T_s with $T_s=1000, 1100, 1200, 1300$. Linewidth (Γ) versus $D^{-3/2}$ plots (inset), with D being the mean crystallite size estimated by Scherrer equation, for LLTO-T with $T=700, 800$ and 900 .

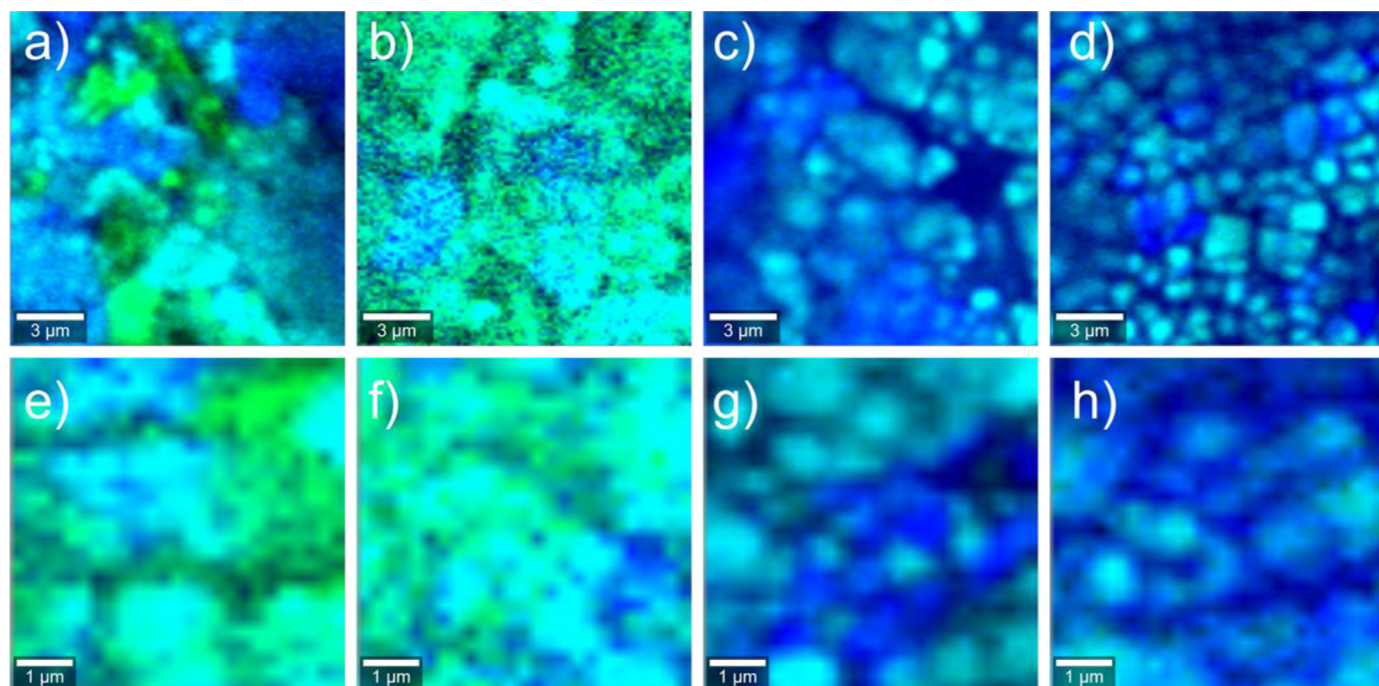


Fig. 5. Confocal Raman imaging for LLTO-900- T_s pellets with $T_s=1000$ (a,e), 1100 (b,f), 1200 (c,g) and 1300 (d,h). Zone A (light blue) was filtered using the LLTO E_g mode ($\sim 120\text{--}180\text{ cm}^{-1}$), zone B (blue) was filtered using the Li_2TiO_3 Ti-O stretching mode ($\sim 650\text{--}690\text{ cm}^{-1}$) and zone C (green) was filtered using the $\text{La}_2\text{Ti}_2\text{O}_7$ F_{2g} mode ($\sim 780\text{--}820\text{ cm}^{-1}$). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

tetragonal $P4/mmm$ to cubic $Pm\bar{3}m$ spacegroup, as also observed by Le Dinh Trong et al. [35].

Confocal Raman spectra for LLTO-900- T_s with $T_s=1000\text{--}1300$

(Fig. 3) showed the progressive disappearance of the impurity peaks, in agreement with XRD analysis. Additionally, a progressive blue shift of the analogous A'_{1g} peak and a red shift of the A_{1g} mode

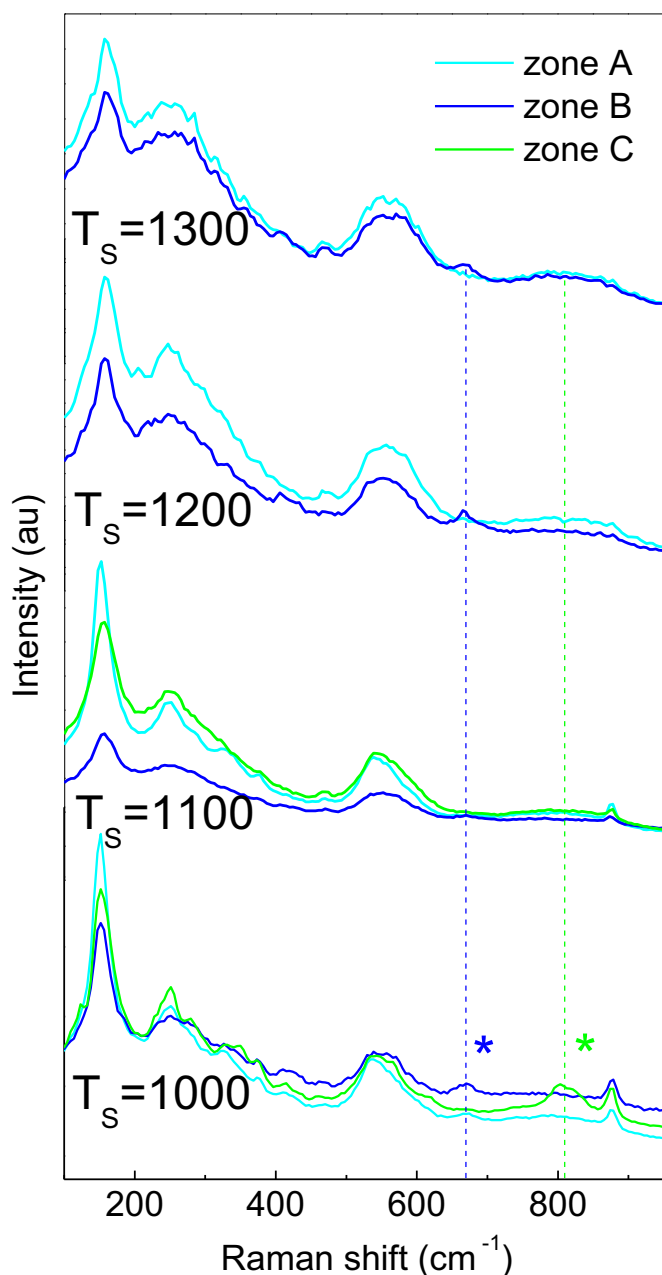


Fig. 6. Confocal Raman spectra for LLTO-900- T_s pellets with $T_s = 1000$ – 1300 . Zones A, B and C are consistent with those defined in Fig. 5. Li_2TiO_3 and $\text{La}_2\text{Ti}_2\text{O}_7$ impurities are marked with blue and green asterisks, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

were observed with increasing T_s , as it is observed in Fig. 4. Moreover, a declining in the intensity of the overall LLTO spectra was observed for $T_s > 1200$, suggesting a transition from the tetragonal $P4/mmm$ to cubic $Pm-3m$ structure, in agreement with the Rietveld analysis discussed previously. However, the presence of broad low intensity peaks for $T_s = 1300$ are suggesting that the Raman inactive $Pm-3m$ cubic structure has a tetragonal distortion or the coexistence with lower amounts of the $P4/mmm$ phase. The drastic lowering in the intensity and broadening of peaks observed above $T_s = 1200$ (Fig. 4b) could be suggesting LLTO phase transition to a distorted-cubic structure or that the remaining tetragonal phase is being reduced to small nanocrystalline domains embedded in the cubic phase. Confocal Raman imaging analysis for LLTO-900- T_s compressed pellets surface (Fig. 5) showed a clear

evidence of the sintering process for $T_s > 1200$, confirming the formation of pure LLTO crystalline phase, with domains ranging between 500–2000 nm. In order to generate the confocal Raman images, three zones were defined based in the presence of impurities. Zone A, associated to pure LLTO zone (cyan in Fig. 5) was obtained by filtering the whole spectra but the E'_g modes region (500 – 600 cm^{-1}) associated to the LLTO perovskite. Zone B, ascribed to a mixture between LLTO and Li_2TiO_3 impurities zone (blue in Fig. 5) was obtained by filtering the whole spectra but the Ti–O stretching mode region (620 – 700 cm^{-1}) ascribed to Li_2TiO_3 phase. Zone C, associated to LLTO with $\text{La}_2\text{Ti}_2\text{O}_7$ impurities zone (green in Fig. 5) corresponding to the F_{2g} mode region (750 – 850 cm^{-1}) of $\text{La}_2\text{Ti}_2\text{O}_7$ phase.

Additionally, Fig. 6 shows the Raman spectra for the pure LLTO zone (zone-A), the LLTO zone with Li_2TiO_3 impurities (zone-B) and the LLTO zone with $\text{La}_2\text{Ti}_2\text{O}_7$ impurities (zone-C). Even though, these impurity peaks have a very low relative intensity, the integrated intensity of Raman spectra is sufficient to create a contrast image. As it is observed in Fig. 5, the presence of Li_2TiO_3 impurities is located at the grain boundaries of LLTO, generating an extra barrier to the lithium transport in LLTO electrolytes. Additionally, confocal Raman images also showed a remarkable increase in the LLTO grain size, especially for $T_s = 1200$ and 1300 specimens. In these cases, grain sizes ranging from $\sim 300\text{ nm}$ to $\sim 1\text{ }\mu\text{m}$ can be observed in Fig. 5g and h, leading to a quantitative approach of the sintering effect on the LLTO microstructure, which was unable to estimate using the Scherrer equation. Thus, confocal Raman spectroscopy appear to be an essential technique to monitor simultaneously the presence of impurities and microstructure giving relevant information for understanding of Li-ion transport in these kinds of electrolytes.

3.4. Raman activity first principles simulation

The starting configuration for the first principles simulation is a supercell of the tetragonal and cubic perovskite unit cells, with the lattice constants fixed at the experimentally determined values shown in Table 1 for $T_s = 1200$ and 1300 , respectively. In both cases, the symmetry was first reduced to $P1$ spacegroup and the after-relaxation structure is shown in Fig. 7. In both cases we observe a distortion from the initial symmetries and a shift on the lithium position from the A-site of the perovskite, as already observed in previous reports [36,37]. Phonons calculation for LLTO in distorted-cubic and tetragonal supercell structures is shown in Table 2. The distortion of the initial symmetries after relaxation revealed the presence of typical LLTO vibrational modes and a low intensity peak at $\sim 878\text{ cm}^{-1}$, which is rarely observed, associated with the symmetric stretching of both Ti–O and Li–O bonds along the x-y plane. Theoretical calculation of Raman activity for the distorted-cubic and tetragonal supercell structures is shown in Fig. 8. The absolute Raman activity of the distorted-cubic supercell structure showed a very low Raman activity in comparison with the tetragonal supercell, as also observed in experimental data for $T_s = 1300$ in relation to $T_s = 1200$, respectively. More interestingly, a drastic lowering in the E_g mode Raman intensity at $\sim 145\text{ cm}^{-1}$ was observed for LLTO distorted-cubic respect to tetragonal supercell structure, as it is shown in Fig. 8. This Raman activity suppression from tetragonal to distorted-cubic phase is in good agreement with experimental Raman spectra analysis, probably suggesting LLTO structural transition from tetragonal to a distorted-cubic structure at $T_s = 1300$.

3.5. Electrochemical impedance spectroscopy (EIS)

LLTO-900- T_s with $T_s = 1100$ – 1300 , studied by means of electrochemical impedance spectroscopy at room temperature,

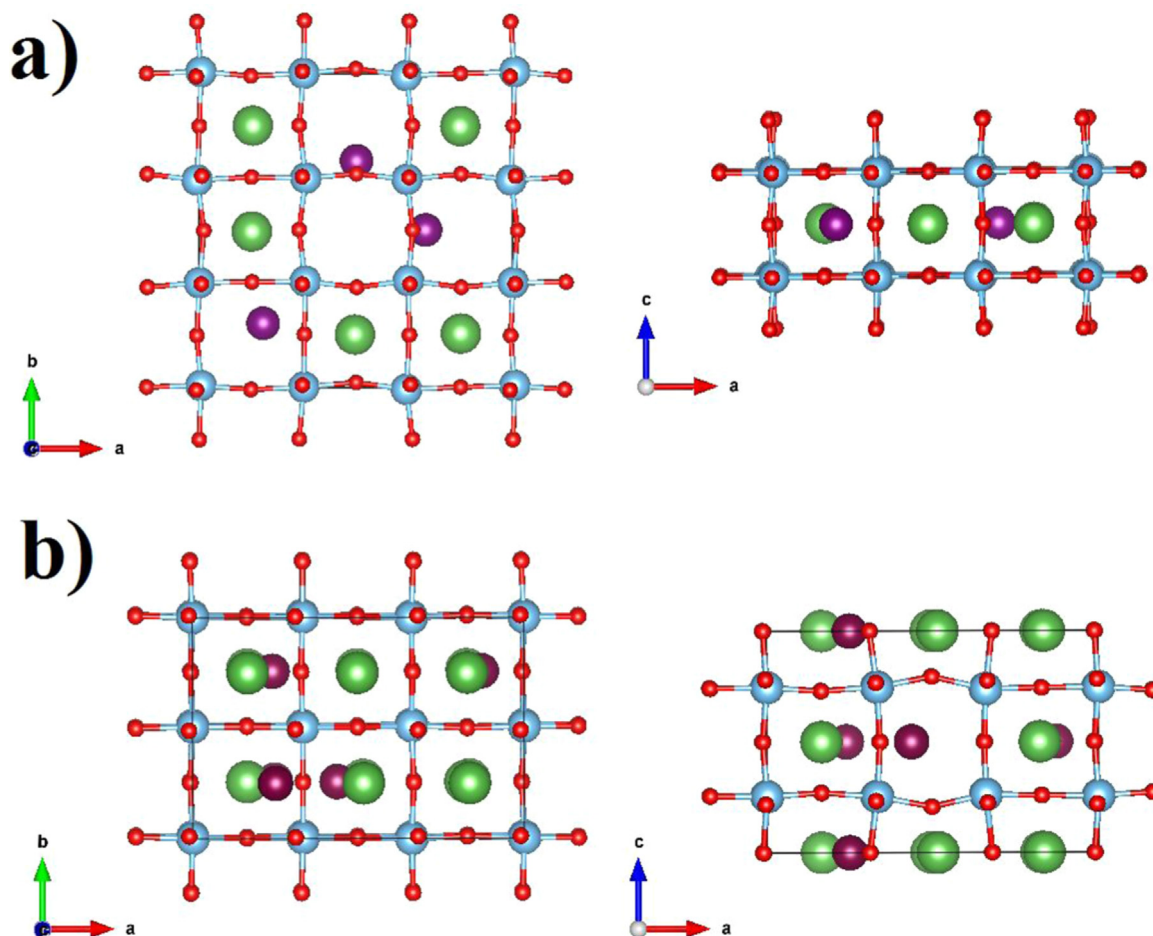


Fig. 7. Theoretical structural models after the ion relaxation of $3 \times 3 \times 1$ distorted-cubic (a) and $3 \times 2 \times 2$ tetragonal (b) supercell structures. References for atoms: lanthanum (green), lithium (purple), titanium (blue) and oxygen (red) [41]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

showed an enhancement in the Li^+ ion conductivity with increasing sintering temperature (T_s). The impedance diagrams plotted in the Nyquist plane (Fig. 9) shows that Li^+ ion mobility in LLTO has two main mechanisms, grain diffusion and grain boundary diffusion that are generally discussed in the literature [31,38]. In the impedance spectra of $T_s=1100$ and 1200 there is an arc circle, attributed to the contribution of the bulk and grain boundary parts, and a straight line related to the polarization of the electrodes where the diffusion blocking of Li^+ ion takes place. These two diagrams can be modeled with the equivalent circuit of the Fig. 8-inset, a Constant Phase Element (CPE) Randless describing the bulk diffusion; and a CPE element Randless with a Warburg element (W) describing the grain boundary. The Nyquist plots of the $T_s=1100$ and 1200 samples showed a better quality fitting when using the Warburg element instead of a series CPE, as usually appears in the literature [12], but the physical meaning of both elements can be attributed to the polarization. In the case of $T_s=1300$ °C sample, the Nyquist plots look very different, described with two arcs attributed to grain and grain boundary diffusion, and there no contribution from polarization, even at low frequency (~ 0.15 Hz). Two different trends were observed, studying the grain and grain boundary contribution to the total conductivity. The first case corresponds to LLTO-900- T_s with $T_s=1100$ and 1200 , where the contribution to the conductivity is higher for grain boundary when compared to the bulk one,

probably due to the low sintering rate. The opposite trend is observed for sample $T_s=1300$, presenting a total conductivity with higher contribution from grain when compared to the grain boundary. In particular, this situations give us the higher total grain conductivity, corresponding to $\sigma_{\text{grain}} = 1.5 \times 10^{-5} \text{ S cm}^{-1}$. The change in the “grain/grain boundary” contributions could be attributed to the sintering process and the crystal phase transition from tetragonal $P4/mmm$ to cubic $Pm-3m$ for LLTO, probably favored by the synthesis conditions. Finally, we would like to mention that the obtained total conductivities showed lower values than $\sigma_{\text{total}} \sim 1 \times 10^{-4} \text{ S cm}^{-1}$ reported in the bibliography [1,15,39]. This could be probably due to the lithium loss at high temperatures and the presence of traces of impurities determined by confocal Raman imaging study. Thus, we are revealing that the formation of impurities at the LLTO grain boundaries is still problematic [40], declining the ion migration and thus reducing the lithium conductivity in these electrolytes.

4. Conclusions

We successfully prepare $\text{Li}_{0.30}\text{La}_{0.57}\text{TiO}_3$ electrolyte by the sol-gel method in acetic medium. Raman spectroscopy showed the formation of lanthanum and titanium acetates precursors, which after calcination lead to formation of the LLTO nanoparticles. The

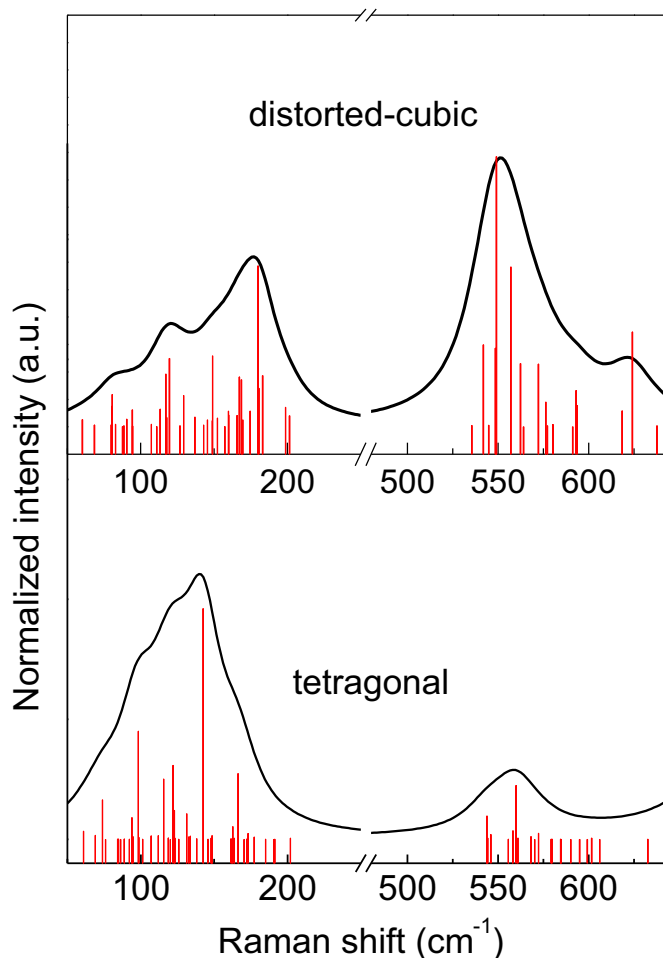


Fig. 8. Raman activity simulation and lorentzian convolution for LLTO in tetragonal and distorted-cubic structure.

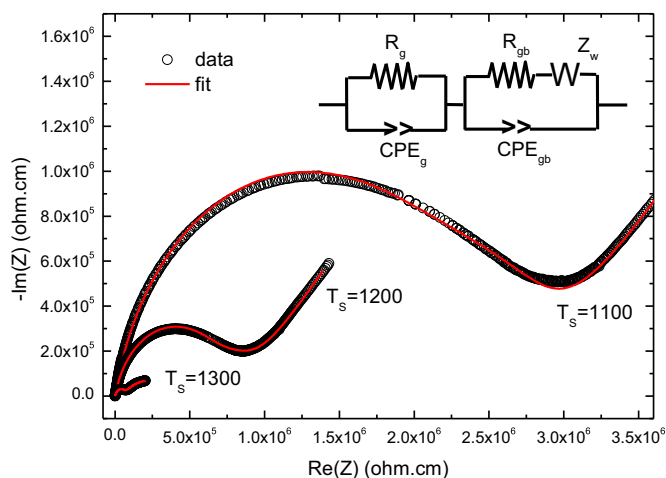


Fig. 9. Nyquist plots for LLTO-900- T_s with $T_s=1100$, 1200 and 1300. The inset shows the circuit model for LLTO-900- T_s with $T_s=1100$ –1200 and $T_s=1300$ (with no Warburg (Z_w) element). Note: “g” indicates grain and “gb” indicates grain boundary.

sintering process, studied by means of confocal Raman imaging technique, evidenced the evolution in the sintering process of LLTO phase together with the progressive disappearance of

impurities as temperature raised. X-ray powder diffraction, with full pattern profile refinements, confirmed no drastic changes in the LLTO perovskite unit cell parameters, but a large increase in the crystallite size domain when increasing sintering temperature. A phase transition for the $\text{Li}_{0.30}\text{La}_{0.57}\text{TiO}_3$ perovskite structure was observed, from tetragonal $P4/mmm$ to distorted-cubic $Pm-3m$ spacegroup, for the highest sintering temperature ($T_s=1300$). The presence of distortions in the cubic phase was evidenced using Raman spectroscopy and correlated with Raman theoretical calculations. In spite of the overall low lithium conductivity, the electrochemical impedance spectroscopy analysis showed a remarkable increase in the lithium bulk conductivity for $T_s=1300$, which can be attributed to the early mentioned crystal phase transition.

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Appendix

The XRD pattern for the LLTO precursor is shown in Fig. A1, to be included in the Appendix section according to the referee suggestion. Lanthanum acetate phase can be easily detected by XRD. However, other minor intensity peaks marked with asterisks could be ascribed to titanium acetate, oxyacetate or other titanium acetate complexes, with no specific stoichiometry, and thus no concluding remarks can be obtained from XRD information available in the literature. We performed a deep search on Powder Diffraction Database (PDF-ICDD), Cambridge Structural Database System (CCDC) and FINDIT (ICSD) database.

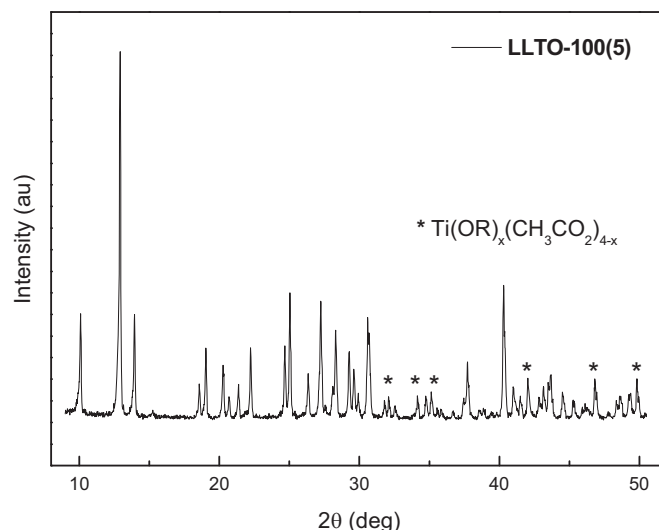


Fig. A1. XRD pattern for LLTO-100(5) precursor.

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