Sol-gel synthesis and structural study of a lithium titanate phase $\text{Li}_{3x}\text{La}_{2/3-x}\square_{1/3-2x}\text{TiO}_3$ as solid electrolyte

Abdelhak Chouiek, Mohamed Naji*, Abdelilah Rjeb, Yahya Ababou and Salaheddine Sayouri
Université sidi Mohamed Ben Abdellah (USMBA)
Laboratoire de Physique Appliquée, Informatique et Statistique (LPAIS), FSDM, B.P.1796, Fès-Atlas, Maroc

*Corresponding author: mohamed.naji3@usmba.ac.ma

Abstract. Perovskite lithium lanthanum titanate (LLTO) was prepared as an inorganic solid electrolyte material for lithium ion batteries applications using sol-gel method. Three different compositions of: (a) $3x=0.3$ ($\text{Li}_{0.3}\text{La}_{0.57}\text{TiO}_3$), (b) $3x=0.5$ ($\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$) were prepared and calcined at 1000°C for 6h, and (c) $3x=0.1$ ($\text{Li}_{0.1}\text{La}_{0.63}\text{TiO}_3$) prepared and calcined at 1100°C for 6h. The effects of lithium content and calcination temperature on the structure of the perovskite powders were studied. The synthesized powders were characterized by X-ray diffraction analysis. Results indicate that the $\text{Li}_{0.3}\text{La}_{0.57}\text{TiO}_3$ was crystallized in tetragonal structure of space group P4/mmm. On the other hand, Rietveld refinement analysis for the LLTO samples confirmed the formation of the $\text{Li}_{0.3}\text{La}_{0.57}\text{TiO}_3$ crystalline phase in the tetragonal P4/mmm space group, the $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$ phase in the tetragonal P4/mmm space group, and $\text{Li}_{0.1}\text{La}_{0.63}\text{TiO}_3$ phase in orthorhombic Pmmm space group.

Keywords
Perovskite; Lithium lanthanum titanate; All-solid-state battery; Sol-gel; LLTO; Refinement.

1. Introduction
All-solid-state batteries lithium are of considerable interest for future technological applications, such as portable electronics, micro-devices and even large-scale applications [1].

Lithium-ion batteries currently represent the main source of power in electronic devices and are widely regarded as one of the most remarkable technologies in transportation electrification. However, lithium-ion batteries still have some limitations, particularly in terms of security. These security problems are often associated with the use of flammable organic electrolytes [2-3].

One of the solutions to these problems is precisely the introduction of solid electrolytes. The advantages of using solid electrolytes instead of organic liquid electrolytes, besides security, are their good thermal stability, higher energy capacity due to the possibility of more compact structures without the need for separators as in the case of conventional batteries, and their wide range of operating temperatures [4].

One of the conditions for the application of the solid electrolyte is that it must have a reasonably higher ionic conductivity. The one potential solid electrolyte is ceramic perovskite ABO$_3$, such as lithium lanthanum titanate, of the formula $\text{Li}_{x}\text{La}_{2/3-x}\square_{1/3-2x}\text{TiO}_3$ called LLTO, ($\square$ represents vacancy) [5]. The highest bulk ionic conductivity reported for LLTO is about $10^{-3}$ S.cm$^{-1}$ at room temperature.
when \(3x = 0.3\) [6], but, the total ionic conductivity of LLTO is low \(10^{-5}\) S.cm\(^{-1}\) due to the low ionic conductivity at the grain boundary [7-8]. Different publications suggest that sintering temperatures, composition (Li to La ratio) and preparation method affect the structure and morphology of LLTO, modifying the resulting conductivity [4-9]. That way, although many reports have been made on the properties of LLTO, different preparation steps and sintering conditions may result in different or improved properties.

LLTO is generally synthesized by the sol-gel method or by solid-state reaction, the latter being easier and more economical. In general, the sintering temperature is above 1250°C, which leads to the evaporation of lithium [10]. In this study, the LLTO samples \(\text{Li}_{3x}\text{La}_{2/3x-1/3x-2x}\text{TiO}_3\) \((3x=0.1; 3x=0.3\) and \(3x=0.5)\) were prepared by the sol-gel method, and characterized by XRD diffraction and their structures were refined using the Rietveld method.

2. Experimental

Figure 1. shows the diagram of the procedure for the synthesis of lithium lanthanum titanate (LLTO) powders. The sol-gel method was used to prepare three different compositions of LLTO for \(3x=0.1; 3x=0.3\) and \(3x=0.5\). The starting materials were lanthanum (III) acetate hydrate \(\text{La(CH}_3\text{COO)}_{3x} \cdot x\text{H}_2\text{O}\) (Sigma-Aldrich, 99% purity), titanium (IV) isopropoxide \(\text{Ti[OCH(CH}_3\text{)}_2\text{]}_4\) (Sigma-Aldrich, 97% purity) and lithium acetate \(\text{Li(CH}_3\text{COO)}_2\text{H}_2\text{O}\) (Sigma-Aldrich, 99% purity) as precursors, lactic acid \(\text{CH}_3\text{CH(OH)COOH}\) (Sigma-Aldrich, 90% purity) as peptizing agent, and distilled water as solvent.

Lanthanum acetate, lithium acetate and titanium sol are mixed in stoichiometric proportions, according to the chemical formulation \(\text{Li}_{3x}\text{La}_{2/3x-1/3x-2x}\text{TiO}_3\) \((3x=0.1; 3x=0.3\) and \(3x=0.5)\) under stirring for 2 hours, to ensure the homogeneity of the final solution. The destabilization of this solution is ensured by evaporation of the solvent in an oven at a temperature of \((60\degree\text{C ~ 70\degree}\)C) for 96 hours. The xerogel obtained is ground in an agate mortar to break up the agglomerates of the powder and increase its reactivity. The mixed powders were calcined at 1000°C (6h) for \((3x=0.3\) and \(3x=0.5)\) and at 1100°C (6h) for \((3x=0.1)\) was calcined.

The obtained samples were analyzed by X-ray diffraction using a computer-controlled XPERT-PRO diffractometer with a copper anode K-Alpha1 \((\lambda_1=1.54060\text{Å})\) and K-Alpha2 \((\lambda_2=1.54443\text{Å})\). A scan was adopted with a 0.0170° step. The chosen measuring range is from 10° to 90°.
3. Results and discussion

3.1. Lithium lanthanum titanate for (3x=0.3) $\text{Li}_{0.3}\text{La}_{0.57}\text{TiO}_3$

The X-ray diffraction patterns of $\text{Li}_{0.3}\text{La}_{0.57}\text{TiO}_3$ obtained by sol-gel after heat treatments at 900°C, 950°C and 1000°C for 6 hours are shown in figure 2.

The formation of the LLTO phase starts at 900°C with impurities. The main impurity is the lanthanum titanate oxide $\text{La}_2\text{Ti}_2\text{O}_7$ which was also found by Bohnke et al [11] during the preparation of $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$ by the sol-gel route and the lithium titanate $\text{Li}_2\text{TiO}_3$ which was found by Romero et al [12] during the preparation of $\text{Li}_{0.3}\text{La}_{0.57}\text{TiO}_3$. When the temperature of the treatment increases, the proportion of impurities decreases, and the calcination temperature at 1000°C promotes the removal of these impurities. $\text{La}_2\text{Ti}_2\text{O}_7$ appears at 700°C as indicated by Kitakoa et al [13].
The structure of Li$_{0.3}$La$_{0.57}$TiO$_3$ heat treated at 1000°C for 6 hours was further refined by means of Rietveld method (Figure 3). In a first step, a refinement was performed using the structural model proposed in the literature by Fourquet et al. [14], which allowed us to verify that the compound is pure LLTO (3x=0.3), and that it crystallizes well in a tetragonal cell (P4/mmm; a=b=3.8704Å and c=7.7621Å and α=β=γ=90°). Reliability factors obtained after refinement ($R_p$=26.80%; $R_{wp}$=20.30%; $R_{exp}$=15.17% and $\chi^2$=1.79). In table 1, the crystallographic characteristics of Li$_{0.3}$La$_{0.57}$TiO$_3$ are presented, and in table 2, the interatomic distances are reported for refined LLTO (3x=0.3), these results are in very good agreement with the literature [15].
Table 1. Wyckoff Sites, Atomic coordinates, for the $P4/nmm$ Structure of Li$_{0.3}$La$_{0.57}$TiO$_3$

| Atom | Site | Atomic coordinates | Occ  |
|------|------|---------------------|------|
|      |      | x   | y   | z   |      |
| La1  | 1a   | 0.00000 | 0.00000 | 0.00000 | 0.05374 |
| La2  | 1b   | 0.00000 | 0.00000 | 0.50000 | 0.02168 |
| Ti   | 2h   | 0.50000 | 0.50000 | 0.26058 | 0.12500 |
| O1   | 1c   | 0.50000 | 0.50000 | 0.00000 | 0.06250 |
| O2   | 1d   | 0.50000 | 0.50000 | 0.50000 | 0.06250 |
| O3   | 4i   | 0.00000 | 0.50000 | 0.24240 | 0.25000 |

Table 2. Interatomic Distances in Å of Li$_{0.3}$La$_{0.57}$TiO$_3$

| Distance                | Occ  |
|-------------------------|------|
| <dTi-O1>                | 2.0226 |
| <dTi-O2>                | 1.8584 |
| 4 × <dTi-O3>           | 1.9403 |
| 4 × <dLa1-O1>          | 2.7368 |
| 8 × <dLa1-O3>          |       |
| 4 × <dLa2-O2>          |       |
| 8 × <dLa2-O3>          |       |
| 2.6991                  | 2.7368 |
| 2.7368                  | 2.7826 |

3.2. Lithium lanthanum titanate for (3x=0.5) Li$_{0.3}$La$_{0.5}$TiO$_3$

For LLTO samples (3x=0.5), the X-ray diffractogram registered on the heat-treated compound at 1000°C is shown in figure 4. The LLTO compound has indeed been formed, with the presence of impurity containing lithium titanate Li$_2$TiO$_3$.

Figure 4. X-ray diffraction of Li$_{0.5}$La$_{0.5}$TiO$_3$ obtained by sol–gel method; (*) peaks of LLTO(3x=0.5); (o) peaks of Li$_2$TiO$_3$
Refinement on the compound synthesized at 1000°C (Figure 5) permitted to obtain the cell parameters 
a=b=3.8703Å and c=7.7529Å using the P4/mmm space group and α=β=γ=90°. Reliability factors are: 
Rp=39.00%, Rwp=26.90%, Rexp=17.15% and χ²=2.46. In table 3, the crystallographic characteristics of 
Li0.5La0.5TiO3 are presented, and in table 4, the interatomic distances for refined LLTO (3x=0.5) are 
reported, these results are confirmed, for example the distances found in reference [15] for Ti-O are in 
the range of those of this study.

Figure 5. Result of the Rietveld refinement performed on the Li0.5La0.5TiO3 phase heat-treated at 
1000°C with calculated and observed diffractograms

| Atom | Site | Atomic coordinates     | Occ    |
|------|------|------------------------|--------|
|      |      | x    | y    | z    |        |
| La1  | 1a   | 0.00000 | 0.00000 | 0.00000 | 0.04368 |
| La2  | 1b   | 0.00000 | 0.00000 | 0.50000 | 0.02515 |
| Ti   | 2h   | 0.50000 | 0.50000 | 0.25542 | 0.13915 |
| O1   | 1c   | 0.50000 | 0.50000 | 0.00000 | 0.12169 |
| O2   | 1d   | 0.50000 | 0.50000 | 0.50000 | 0.16456 |
| O3   | 4i   | 0.00000 | 0.50000 | 0.24422 | 0.34141 |

Table 4. Interatomic Distances in Å of Li0.5La0.5TiO3

| <dT1-O1> | <dT1-O2> | 4×<dT1-O3> | 4×<dLa1-O1> |
|----------|----------|------------|-------------|
| 1.9803   | 1.8962   | 1.9371     | 2.7367      |

| 8×<dLa1-O3> | 4×<dLa2-O2> | 8×<dLa2-O3> |
|-------------|-------------|-------------|
| 2.7074      | 2.7367      | 2.7708      |
3.3. Lithium lanthanum titanate for (3x=0.1) \( \text{Li}_{0.1}\text{La}_{0.63}\text{TiO}_3 \)

For samples \((3x=0.1)\), the formation of the LLTO phase is produced at 900°C, but with impurities. We have therefore tried to increase the heat treatment temperature to 1000°C in order to obtain pure phases, but unfortunately, we still also observe the presence of lanthanum and titanium oxide \(\text{La}_2\text{Ti}_2\text{O}_7\) in greater or lesser quantities. The addition of 10% excess of lithium acetate allows us to reduce the quantity of these impurities without eliminating them entirely, an excess of 10% of lithium was added to the stoichiometric mixtures to compensate for lithium loss during processing [16]. (Figure 6).

![Figure 6. X-ray diffraction of Li\(_{0.1}\)La\(_{0.63}\)TiO\(_3\) obtained by sol–gel method; (*) peaks of LLTO(3x=0.1) ; (+) peaks of La\(_2\)Ti\(_2\)O\(_7\) The Li\(_{0.1}\)La\(_{0.63}\)TiO\(_3\) compound heat treated at 1100°C with the 10% excess of lithium acetate was used to perform a Rietveld refinement using the FullProf program (Figure 7). Using the structural model proposed by Ibarra et al [15], we have verified that the LLTO compound \((3x=0.1)\), crystallizes well in an Orthorhombic cell (Pmmm; \(a=3.8743\text{Å}\); \(b=3.8632\text{Å}\) and \(c=7.7816\text{Å}\), and \(\alpha=\beta=\gamma=90°\)), and the factors of reliability are: \(R_p=39.40\%\), \(R_{wp}=30.40\%\), \(R_{exp}=23.93\%\) and \(\chi^2=1.61\). In table 5, the crystallographic characteristics of Li\(_{0.1}\)La\(_{0.63}\)TiO\(_3\) are presented, and in table 6, the interatomic distances for refined LLTO \((3x=0.1)\) are reported, these results are in very good agreement with the literature [15].

![Figure 7. Result of the Rietveld refinement performed on the LLTO (3x=0.1) phase heat-treated at 1100°C with the 10% excess of lithium acetate]
Table 5. Wyckoff Sites, Atomic coordinates, for the \textit{Pmmm} Structure of Li$_{0.1}$La$_{0.63}$TiO$_3$  

| Atom | Site | Atomic coordinates  | Occ  |
|------|------|---------------------|------|
|      |      | $x$   | $y$   | $z$    |      |
| La1  | 1a   | 0.00000 | 0.00000 | 0.00000 | 0.11467 |
| La2  | 1c   | 0.00000 | 0.00000 | 0.50000 | 0.04715 |
| Ti   | 2t   | 0.50000 | 0.50000 | 0.26272 | 0.25000 |
| O1   | 1f   | 0.50000 | 0.50000 | 0.00000 | 0.12500 |
| O2   | 1h   | 0.50000 | 0.50000 | 0.50000 | 0.12500 |
| O3   | 2r   | 0.00000 | 0.50000 | 0.23426 | 0.25000 |
| O4   | 2s   | 0.50000 | 0.00000 | 0.25075 | 0.25000 |

Table 6. Interatomic Distances in Å of Li$_{0.1}$La$_{0.63}$TiO$_3$  

|       | <dTi-O1> | <dTi-O2> | 2 × <dTi-O3> | 2 × <dTi-O4> | 4 × <dLa1-O1> |
|-------|----------|----------|-------------|-------------|--------------|
|       | 2.0444   | 1.8464   | 1.9498      | 1.9338      | 2.7356       |

|        | 4 × <dLa1-O3> | 4 × <dLa1-O4> | 4 × <dLa2-O2> | 4 × <dLa2-O3> | 4 × <dLa2-O4> |
|--------|--------------|--------------|-------------|-------------|--------------|
|       | 2.6559       | 2.7495       | 2.7356      | 2.8297      | 2.7413       |

4. Conclusion  
The samples of lithium titanate and lanthanum titanate LLTO with (3x=0.1), (3x=0.3) and (3x=0.5); were synthesized by the sol-gel method. The Li$_{0.3}$La$_{0.57}$TiO$_3$ phase was shown to crystallize in the tetragonal structure (space group P4/mmm). The Li$_{0.5}$La$_{0.5}$TiO$_3$ phase has been indexed in a tetragonal cell (P4/mmm space group). While the Li$_{0.1}$La$_{0.63}$TiO$_3$ phase was crystallized in an Orthorhombic cell (Pmmm space group).

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