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Local structure of the Li$_{1/8}$La$_{5/8}$TiO$_3$ (LLTO) ionic conductor by theoretical simulations

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Abstract. Some locally ordered arrangements of the lithium-lanthanum-vacancy distribution were devised, within the disordered perovskite superstructure of the Li$_{1/8}$La$_{5/8}$TiO$_3$ ion conductors. By consideration of the Li$_{1/8}$La$_{5/8}$TiO$_3$ composition, two ordered superstructures are built up on the basis of 8 formula units/primitive cell (with monoclinic Pm space group symmetry). Periodic quantum-mechanical calculations were carried out at the B3LYP level by the CRYSTAL06 code, using ECP for lanthanum and all-electron basis sets for all other atoms. For each ordered model the complete structure was fully relaxed by energy minimization, finding that the 4La/1La+1Li+2 arrangement is more stable than 3La+1/2La+1Li+1. Hence the average disordered Cmmm structures of Li$_{0.16}$La$_{0.613}$TiO$_3$ and Li$_{0.18}$La$_{0.607}$TiO$_3$ (neutron diffraction data) can be rationalized. The optimized Li positions were found to lie in peripheral sites within the A-type cavities, close to separating windows and in flattened square-pyramidal coordination. Some ambiguous aspects of the corresponding results of diffraction experiments can then be clarified.

1. Introduction
Lithium perovskites have attracted a lot of attention in search of inorganic materials displaying a high lithium ion mobility [1]. This is largely related to the peculiar flexibility of the ABO$_3$ perovskite structure type, that is able to distort in a great variety of ways under the effect of physical (temperature, pressure) and chemical (compositional changes in the A and B sites) parameters. Such distortions, coupled with charge imbalance due to chemical substitutions in the cation sites, can provide lithium ions with multiple available sites of comparable energy, so as to promote disorder and then improve the ion mobility.

The Li$_{1/8}$La$_{2/3}$TiO$_3$ system, with perovskite-type structures, is one of those showing the highest lithium ion electrical conductivity at room temperature (about 10$^{-3}$ S cm$^{-1}$ for $x = 0.3$) [2,3]. Unfortunately, this excellent ionic conductor cannot be used as a solid electrolyte in the design of an ordinary Li battery, because of the high chemical reducibility of the Ti$^{4+}$ ions when LLTO is placed in contact with Li metal electrodes. It can however be employed in other electrochemical devices, and it is especially important as model material to understand the reasons of high ionic conductivity and to design new conductive systems.

In Li-free La$_{2/3}$TiO$_3$, lanthanum occupies on the average 2/3 of the A sites of the ABO$_3$ perovskite structure, whereas 1/3 are vacant [4]. Lithium insertion occurs by partly replacing La atoms, and partly occupying the hollows around the empty A sites; when $x=0.5$, all the A sites are saturated by either La or Li. Clearly, the extended disordered distribution of lithium atoms and vacancies is responsible for the high ionic mobility. However, although several structural studies of this system at a number of Li compositions have been performed, only in a few cases lithium could be
located and/or refined by neutron diffraction [5-11]. This task is particularly difficult in case of small Li content (say, x < 0.25), where a problem of scattering sensitivity arises.

Several types of symmetry lowering, with different superlattices with respect to the basic perovskite cubic cell (a₀ edge), were found by experimental studies [1]. The lithium content (x value) and the cooling rate in the sample synthesis play a crucial role in this respect. For samples with low Li content (0.12 ≤ x ≤ 0.20), an orthorhombic Cmmm phase with cell of type 2a₀×2a₀×2a₀ was found, in case of synthesis by slow cooling from high temperature [7,8]. A particular interest is shown by the intermediate x=0.3 composition, because of its very good ionic conductivity performance. Two detailed neutron studies of the Li$_{0.7}$La$_{0.56}$TiO$_3$ composition were performed recently by our group, on a slowly cooled sample [10] and on one quenched into liquid nitrogen [9]. Both of them gave a tetragonal $\sqrt{2}$a₀×$\sqrt{2}$a₀×2a₀ unit-cell, but with different space group symmetries (P4/nbm and I4/mcm, respectively), and different structure details. In particular, the Li atom positions could be determined and refined successfully, yielding quite reasonable Li-O distances with a fourfold coordination environment. It was confirmed that by X-ray diffraction the superlattice peaks transforming $a_0^c$×$a_0^c$×2a₀ into $\sqrt{2}a_0^c$×$\sqrt{2}a_0^c$×2a₀ are missed completely. Another investigation, carried out on the x=0.36 composition, proposed instead an orthorhombic Cmmm structure similar to that found for Li-poor terms [11].

Independently of symmetry and compositional features, two main distortions are observed, at least in unquenched LLTO samples at room temperature, with respect to the ideal perovskite structure. First, a partial ordering of the La-Li-ion distribution in the A cages is observed along the z axis; this makes the c cell edge to double from a₀ to 2a₀, so that alternate (001) layers of La-rich and La-poor A-type sites arise. Second, the TiO$_6$ octahedra tilt in anti-phase sequence around at least one of the crystallographic axes, which is z for tetragonal structures [9,10] (a'd'c' scheme, according to Glazer's notation [12]), and usually y for orthorhombic structures [7,8,11] (a'b'c' scheme). An enlargement of the unit-cell in the (001) plane from a₀×a₀ to $\sqrt{2}$a₀×$\sqrt{2}$a₀ (tетragonal) or to 2a₀×2a₀ (orthorhombic) ensues. The partial ordering along the z axis is sensitive to temperature [13,14]; quenched samples of the tetragonal Li$_{0.7}$La$_{0.56}$TiO$_3$ composition keep the high-temperature full disorder of the La/Li pair, which are distributed in a single A-type site (I4/mcm symmetry) [9].

However, although a sufficiently clear picture of the complex structural properties of LLTO phases begins presently to be outlined, this is limited to statistically averaged configurations, such as those compatible with diffraction experiments. Solid state NMR investigations of the Li$^+$ ion dynamics in LLTO were indeed performed [15], detecting the presence of ions of two kinds with slightly differing environments, but much more detailed information on local scale is needed to untangle the complex disorder of the La-Li- ion distribution in the A cages. To achieve this goal, theoretical simulations of ordered arrangements of the LLTO structure, by state-of-the-art first principles calculations of total energy, have been undertaken. Following some preliminary work performed on the Li$_{1/2}$La$_{1/2}$TiO$_3$ and Li$_{1/6}$La$_{11/6}$ TiO$_3$ compositions [16], the new Li$_{1/2}$La$_{13/8}$ 1/4TiO$_3$ term is here included, so as to cover all three main classes of Li-rich, Li-intermediate and Li-poor LLTO phases, respectively.

2. Method of calculation
All quantum-mechanical calculations were carried out by the computer code CRYSTAL06 [17], implementing a periodic LCAO (Linear Combination of Atomic Orbitals) approach and employing either the DFT (Density-Functional-Theory) or the Hartree-Fock Hamiltonian, or even mixtures of them. In this case the B3LYP hybrid functional was used, including the DFT-LYP non local correlation [18] and a mixture of the DFT Becke’s [19] with the Hartree-Fock exchange. All-electron localized basis sets of Gaussian-type functions were employed for the radial parts of the AO’s of Ti, O and Li, corresponding to the schemes 8(s)6s4p11(sp)31(d)G, 8(s)4p11(sp)G, and 6(s)1(sp)G, respectively. For the La atom, an ECP [20] was used to account for internal electrons, with a 4p11(sp)21(d)G basis set for valence electrons. The exponents of the outer Gaussians were optimized by energy minimization of the simplest ordered model of Li$_{0.5}$La$_{0.5}$TiO$_3$, with the experimental structural parameters. The reciprocal space was sampled according to a regular sublattice defined by 4
points in each direction of the Monkhorst grid. The five tolerances related to cut-off limits for series summation were set to $10^{-7}$, $10^{-7}$, $10^{-7}$, $10^{-7}$, and $10^{-14}$. Convergence was also controlled by a $\Delta E$ threshold of $10^9$ hartree per primitive unit cell in the SCF cycles. In order to accelerate the SCF convergence, the technique of level shifter was used, enhancing the energy difference between highest occupied and lowest empty states in the first cycles. Atomic coordinates were optimized by calculation of analytical gradients and subsequent conjugate gradients algorithm (OPTCOORD option).

3. Results and discussion

For the Li$_{1/8}$La$_{5/8}$TiO$_3$ composition, selected as representative of Li-poor LLTO phases, two ordered structural models were devised within a $2a_p \times 2a_p \times 2a_p$ perovskite supercell ($Z = 8$ f.u, two (001) layers with four A-type sites/cell each). In both cases a single mirror plane was kept (monoclinic $Pm$ space group), so as to reduce symmetry constraints to a minimum. Models (i) and (ii) are based on the 4La/1La+1Li+2 and 3La+1/2La+1Li+1 sequences, respectively (figure 1). Symbols are adopted according to the following convention: 2La+1Li+1 means a layer with 4 A-type sites/2D-cell, of which two are occupied by lanthanum, one by lithium and one is vacant. The only other ordered arrangement consistent with the 2$a_p \times 2a_p \times 2a_p$ supercell, 3La+1Li/2La+2, was discarded because Li is therein trapped in a A hollow surrounded by La atoms, with no possible mobility within the corresponding layer.

Figure 1 Views of the ordered models of the Li$_{1/8}$La$_{5/8}$TiO$_3$ structure used in the calculations. Large pale and dark spheres represent O and La atoms, respectively; Li atoms are denoted as small grey balls, and TiO$_6$ coordination octahedra are emphasized. The unit-cell is a supercell $2a_p \times 2a_p \times 2a_p$ of simple perovskite ($Z = 8$ f.u.), with $Pm$ monoclinic symmetry. La/Li ordering is achieved within the two independent (001) layers of A-type hollows, containing 4La (below) and 1La+1Li+2 (above) in case (i), and 3La+1 (below) and 2La+1Li+1 (above) in case (ii).

3.1. Least-energy optimizations

Least-energy structure optimizations were performed at first with a fixed tetragonal ($a = b$) unit-cell taken from experimental results of Li$_{0.3}$La$_{0.567}$TiO$_3$ [10], relaxing all atomic fractional coordinates within the $Pm$ symmetry (26 atoms in the unit-cell). Then also the unit-cell constants were relaxed,
keeping the orthorhombic geometry ($\alpha=\beta=\gamma=90^\circ$). The energy values obtained, and the lattice constants employed or calculated in each case are reported in table 1.

A modest increase of the unit-cell edges (1.0 to 1.5%) is brought about by lattice relaxation. The values obtained can be best compared to the experimental results of the two closest compositions $\text{Li}_{1.16}\text{La}_{0.615}\text{TiO}_3$ [7] and $\text{Li}_{1.18}\text{La}_{0.607}\text{TiO}_3$ [8], orthorhombic $\text{Cmmm}$ (table 1). However, it turns out that the mirror plane normal to the monoclinic $y$ axis of the optimized models corresponds to the $m$ plane of the experimental $\text{Cmmm}$ structure which is perpendicular to the $x$ axis. Therefore, the $a$ and $b$ unit-cell edges have to be exchanged for a correct comparison between least-energy and experimental results in table 1. On taking this care, the slight difference between the $a$ and $b$ lengths observed for both the $\text{Li}_{1.16}\text{La}_{0.615}\text{TiO}_3$ and $\text{Li}_{1.18}\text{La}_{0.607}\text{TiO}_3$ compositions ($a < b$ in the $\text{Cmmm}$ reference) appears to be correctly reproduced by the least-energy relaxation of both models considered ($a > b$ in the $\text{Pnnm}$ reference). This confirms that the ordered arrangements selected are fully consistent with the average experimental structure of Li-poor LLTO.

Model (i) appears to be definitely preferred energetically over model (ii), with a $\Delta E$ gain of -0.125 or -0.127 eV according to whether the cell is relaxed or not. This result, substantially unaffected by lattice optimization, agrees with what found previously for the $\text{Li}_{1.125}\text{La}_{0.625}\text{TiO}_3$ composition [16], where the fully ordered $4\text{La}/4\text{Li}$ arrangement had energy differences of -0.095 and -0.169 eV with respect to models $3\text{La}+1\text{Li} / 1\text{La}+3\text{Li}$ and $2\text{La}+2\text{Li} / 2\text{La}+2\text{Li}$. It can be easily shown that the relative stability of the two ordered arrangements is unaffected by consideration of the configurational entropy.

**Table 1.** Unit-cells used or optimized in the simulations of $\text{Li}_{1.125}\text{La}_{0.625}\text{TiO}_3$, compared to experimental values for similar LLTO compositions. The corresponding energies obtained are reported.

| Model | Structure | $a$ (Å) | $b$ (Å) | $c$ (Å) | $E$ (hartree/f.u.) |
|-------|-----------|---------|---------|---------|------------------|
| Model (i) | 4La/1La+1Li+2 | 7.7522 | 7.7522 | 7.7464 | -1096.05317 |
| Model (ii) | 3La+1 | 7.8280 | 7.8115 | 7.9022 | -1096.05528 |
| Model (ii) | relaxed cell | 7.8280 | 7.8115 | 7.9022 | -1096.05528 |
| Exp. $\text{La}_{0.18}\text{La}_{0.013}\text{TiO}_3$ [7] | (a and b exchanged) | 7.8758 | 7.8574 | 7.8574 | -1096.05067 |
| Exp. $\text{La}_{0.18}\text{La}_{0.007}\text{TiO}_3$ [8] | (a and b exchanged) | 7.740 | 7.718 | 7.771 | -1096.05245 |

Every structural arrangement within the $2a_x \times 2a_y \times 2a_z$ supercell can be characterized by its multiplicity $p = \frac{p_1}{p_2}$, where $p_1$ and $p_2$ are the $4!/n(La)!n(Li)!n(\text{Ti})!$ values for each of the two layers, so that a configurational entropic term of $(\text{Rln} p)/8$ per f.u. ensues. Thus, models (i) and (ii) have multiplicities $1 \times 12 = 12$ and $4 \times 12 = 48$, respectively, and a free energy difference $\Delta F(\text{ii-i}) = 12237.1447$ Jmol$^{-1}$ can be obtained from the $\Delta E(\text{ii-i})$ and $\Delta S(\text{ii-i})$ values. It turns out that the gain of configurational entropy achieved by model (ii) over (i) is not sufficient to counterbalance its higher energy at any reasonable temperature. Therefore, at least by the approximation of neglecting possible differences of vibrational free energy, we can conclude that the more ordered local arrangement of type (i) should be substantially more populated than that of type (ii) within the average structure of $\text{Li}_{1.125}\text{La}_{0.625}\text{TiO}_3$. Model (i) corresponds to La occupancies of 1.0 and 0.25 in the first and second layer, respectively, and the corresponding values for model (ii) are 0.75 and 0.5. The Rietveld-refined occupancies of the two independent La sites in the $z=0$ and $z=0.5$ layers of the $\text{Cmmm}$ structure are 0.939 and 0.301 for $\text{Li}_{1.16}\text{La}_{0.615}\text{TiO}_3$ [7], and 0.962 and 0.258 for $\text{Li}_{1.18}\text{La}_{0.607}\text{TiO}_3$ [8], fully confirming that both experimental structures are much closer to model (i) than (ii).

The complete listing of atomic fractional coordinates optimized for the two models (fixed cell of table 1) is reported in table 2. By careful inspection of the coordinates of model (i), the presence of an
additional (001) mirror plane passing through the layers of the A-type sites (at \( z = 1/4 \) and 3/4) can be detected, so that the true symmetry proves to be \( P2\overline{1}m \) rather than \( Pm \). This was confirmed by re-optimizing the structure in the orthorhombic space group: no significant changes of the energy or of the fractional coordinates were observed. However, the \( Pm \) coordinates have been left for better comparison with model (ii), where the symmetry is not increased.

**Table 2.** Least-energy atomic fractional coordinates calculated for the 4La/1La+1Li+2 \( (i) \) and 3La+1 /2La+1Li+1 \( (ii) \) models of \( \text{Li}_{1/8}\text{La}_{5/8}^{1/4}\text{TiO}_3 \)

|       | Model (i)    | Model (ii)   |
|-------|--------------|--------------|
|       | \( x \)      | \( y \)      | \( z \)      | \( x \)      | \( y \)      | \( z \)      |
| La1   | 0.00000      | 0.00000      | 0.25000      | 0.00000      | 0.00000      | 0.25000      |
| La2   | 0.01058      | 0.50000      | 0.24992      | 0.02242      | 0.50000      | 0.25053      |
| La3   | 0.50301      | 0.00000      | 0.24993      | 0.49791      | 0.00000      | 0.25502      |
| La4   | 0.49388      | 0.50000      | 0.24977      | 0.99961      | 0.50000      | 0.25037      |
| La5   | 0.01172      | 0.50000      | 0.74993      | 0.49660      | 0.50000      | 0.75039      |
| Ti1   | 0.25788      | 0.75656      | 0.98602      | 0.25434      | 0.75589      | 0.99729      |
| Ti2   | 0.74579      | 0.24955      | 0.98982      | 0.74376      | 0.25042      | 0.00454      |
| Ti3   | 0.25779      | 0.75654      | 0.51377      | 0.25390      | 0.75579      | 0.50866      |
| Ti4   | 0.74566      | 0.24953      | 0.50994      | 0.74398      | 0.24964      | 0.50361      |
| O1    | 0.25040      | 0.00000      | 0.03364      | 0.25624      | 0.00000      | 0.02939      |
| O2    | 0.75474      | 0.50000      | 0.02696      | 0.76999      | 0.50000      | 0.99942      |
| O3    | 0.24442      | 0.50000      | 0.99736      | 0.22832      | 0.50000      | 0.99753      |
| O4    | 0.75767      | 0.00000      | 0.98994      | 0.74404      | 0.00000      | 0.00432      |
| O5    | 0.00239      | 0.73977      | 0.01568      | 0.99849      | 0.75088      | 0.02047      |
| O6    | 0.50279      | 0.75124      | 0.02102      | 0.49857      | 0.74240      | 0.00195      |
| O7    | 0.25395      | 0.73345      | 0.24988      | 0.24116      | 0.75282      | 0.25470      |
| O8    | 0.75227      | 0.22622      | 0.24994      | 0.74919      | 0.22624      | 0.25551      |
| O9    | 0.24352      | 0.50000      | 0.50260      | 0.24954      | 0.50000      | 0.51213      |
| O10   | 0.75671      | 0.00000      | 0.51006      | 0.75886      | 0.00000      | 0.50694      |
| O11   | 0.25102      | 0.00000      | 0.46614      | 0.24051      | 0.00000      | 0.47939      |
| O12   | 0.75549      | 0.50000      | 0.47325      | 0.74386      | 0.50000      | 0.52088      |
| O13   | 0.00240      | 0.74074      | 0.48393      | 0.99735      | 0.72698      | 0.49241      |
| O14   | 0.50271      | 0.75055      | 0.47872      | 0.49832      | 0.75710      | 0.50637      |
| O15   | 0.23369      | 0.75179      | 0.74990      | 0.24604      | 0.72786      | 0.75431      |
| O16   | 0.77797      | 0.26117      | 0.74991      | 0.75194      | 0.25656      | 0.75573      |
| Li    | 0.83903      | 0.00000      | 0.74987      | 0.76683      | 0.00000      | 0.75572      |

3.2. Ordered models and experimental average structure

In order to evaluate the structural details of the two ordered models, also in comparison with the corresponding features of the experimental average structures, it is convenient to examine the (001) projections of the two model layers (figure 2a-d) and of the single disordered layer of \( \text{Li}_{0.16}\text{La}_{0.613}\text{TiO}_3 \)
Model (i): (a) 4La layer                (b) 1La+1Li+2 layer
Model (ii): (c) 3La+1 layer      (d) 2La+1Li+1 layer
(e) Cmmm average structure from neutron diffraction [7]

Figure 2. Optimized least-energy configurations of the two (001) layers of each ordered model of the Li<sub>1/8</sub>La<sub>5/8</sub>TiO<sub>3</sub> structure (a-d), and disordered layer of the experimental structure [7] of Li<sub>0.16</sub>La<sub>0.613</sub>TiO<sub>3</sub> (e).

(figure 2e). The Cmmm experimental structure is rotated by 90° around z, so as to have correspondence between its (100) mirror plane and the (010) one of the ordered models; further, the axis origin has been shifted by 1/4 along y for consistency with the models. The disordered arrangement of La and Li atoms within the A-type cages of the average structure is clearly visible in figure 2e. A close structural similarity appears between the (e) and (a) octahedral frameworks: in particular, the 4La layer of model (i) shows additional (100) mirror planes at x=1/4 and 3/4, which correspond exactly to the (010) planes of the Cmmm structure. Further, the octahedral tilt of type a<sup>0</sup>b<sup>0</sup>c<sup>0</sup> [12] around the y axis, observed in the experimental structure, is also found as a<sup>b</sup>c<sup>0</sup> rotation around x in the 4La layer. These features are not present in the La-poor 1La+1Li+2 layer of model (i), so that the octahedral framework of the Cmmm configuration seems to match that of the more populated La-rich layer only of such a model. On the other hand, in both layers of model (ii) an a<sup>0</sup>d<sup>c</sup> tilt scheme is observed, similar to that of the P4/nbm structure of Li<sub>0.3</sub>La<sub>0.567</sub>TiO<sub>3</sub> rather than to the Cmmm arrangement of the Li-poor compositions. This agrees with the previous energetic findings that model (i) is more stable than model (ii).

3.3. Location and bonding environment of Li atoms
Out of all details of chemical bonding geometry which can be derived, those concerning the Li atom environment are most important. In both models, lithium appears to be located at about the z level of the La and empty A sites of the upper (001) layer, but in a peripheral position with respect to the
cavity centre (0, 0, 3/4), close to the centre of the (100) O₄ square window separating adjacent A cavities (3/4, 0, 3/4, cf. figures 1 and 2b, 2d). In case of model (i), this location corresponds to the S1 site determined experimentally in the structure of Li₀.607La₄TiO₃ [9,10] and found by least-energy calculations in the ordered models of the Li₂La₁₂TiO₄ and Li₀.67La₀.33 1/8 TiO₃ compositions [16]. For model (ii), Li is located very close to site S3 at the window centre. Sites S1 and S3 are the most relevant ones for the process of Li⁺ ion transfer involved in ionic conductivity [9-11,16, 21].

The experimental structural studies of Li₀.16La₀.61TiO₃ [7] and Li₀.18La₀.60TiO₃ [8] show Li in slightly displaced positions. In the former case, the published coordinates 0, 0.189, 0.398 have to be transformed by a y-1/4, z+1/4 origin shift followed by the exchange of the x,y coordinates, in order to be consistent with the Pm reference of table 2. We thus obtain 0.939, 0, 0.648, which is a position closer to the cavity than to the window centre (cf. figure 2c). In the Li₀.18La₀.607TiO₃ case, on the other hand, the Li atoms are reported to be located exactly at the window centres. These slightly inconsistent experimental results for two very similar compositions, and for the same Cmmm basic structure, could be related to the difficulties of locating and refining the Li atom positions even by neutron diffraction, owing to the comparatively small scattering length and high absorption coefficient of that atom. The Li position optimized for model (i) would correspond to coordinates 0, 0.0890, 0.4999 with respect to the original coordinate reference of the literature [7,8,11], and is closer to Li2 of ref. [8] at the window centre than to Li of ref. [7].

Table 3. Li-O bond distances (Å) for the two ordered models of Li₁/₈La₈/₈ 1/4 TiO₃ and for the experimental structures of two similar compositions.

| Li₁₀.₁₂₅La₀.₆₂₅TiO₃ model (i) | Li | 1.964 ×2 | 2.079 ×2 |
| Li₁₀.₁₂₅La₀.₆₂₅TiO₃ model (ii) | Li | 1.944 | 1.967 | 1.996 ×2 |
| Li₀.₁₆La₀.₆₂₂TiO₃ | Cmmm [7] | Li | 2.05 | 2.36 ×2 | 2.64 |
| Li₀.₁₈La₀.₆₁TiO₃ | Cmmm [8] | Li1 | 1.79 | 1.94 ×2 | 2.10 |
| | | Li2 | 1.94 ×2 | 2.07 ×2 |

In table 3, the bonding environment of Li atoms is reported for the optimized model (i) and (ii), and it is compared to the neutron diffraction results for the Li₀.₁₆La₀.₆₂₂TiO₃ and Li₀.₁₈La₀.₆₁TiO₃ compositions. A quite flattened square pyramidal coordination appears, with respect to the four O atoms forming the (100) window centred at 3/4, 0, 3/4 (figure 2), showing regular Li-O bond distances. This flat coordination geometry can favour the Li⁺ ion mobility through the window by means of a mechanism of ‘umbrella inversion’ of the pyramid. The Li surrounding of the experimental structure of Li₀.₁₆La₀.₆₁TiO₃ is not very different, whereas in the Li₀.₁₈La₀.₆₁TiO₃ case we observe a quite distorted 3+1 coordination geometry, which seems to be less reliable as discussed above.

4. Conclusions

Accurate calculations of quantum-mechanical total energy have been performed for ordered structural models of the Li₀.₁₂₅La₀.₆₂₅TiO₃ phase, representative of Li-poor compositions within the LLTO system. This has proved to be a powerful tool for understanding the local atomic arrangement in the disordered average structures determined by diffraction experiments. In particular, it has been shown that Li atoms and vacancies tend to be ordered in a single La-poor layer (1La+1Li+2 ) alternating with a La-full layer (4La), giving rise to the energetically favoured local arrangement. The contribution of configurational entropy is not able to counterbalance this result.

As important outcome of structural optimizations, the Li atoms have been located in least-energy sites close to the centres of O₄ windows separating adjacent A-type hollows. This result is in agreement with Rietveld refinements of the Li-richer Li₀.₃₃La₀.₆₇TiO₃ composition, and in part with those of Li₀.₁₈La₀.₆₁TiO₃, but it differs significantly from the Li locations reported for the closer
$\text{Li}_0.16\text{La}_{0.62}\text{TiO}_3$ composition. Therefore, owing to the experimental difficulties of locating Li atoms accurately, least-energy optimizations can be very helpful to assess the reliability of such results, also in view of their importance for understanding the mechanisms of Li$^+$ ion transfer.

Calculations of the energy barriers along the ion mobility pathways are now in progress, in order to determine the most favoured mechanism and to simulate the activation parameters of the conduction process.

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