



Reassessing the structure of the sorbent with nominal composition $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ used for direct Lithium extraction

Martina Gamba^{a,b,*}, Laura Herrmann^{a,c}, Björn Schwarz^a, Hang Li^a, Stefan Mangold^d, Sylvio Indris^{a,e}, Helmut Ehrenberg^a, German Lener^{f,g}, Fabian Jeschull^{a,*}

^a Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), 76344 Eggenstein-Leopoldshafen, Germany

^b CETMIC, Centro de Tecnología de Recursos Minerales y Cerámica (CONICET La Plata CIC PBA, UNLP), Camino Pque. Centenario y 506 (1897), M. B. Gonnet, Argentina

^c R&D Department, EnBW Energie Baden-Württemberg AG, Durlacher Allee 93, 76131 Karlsruhe, Germany

^d Karlsruhe Institute of Technology (KIT), Institute for Photon Science and Synchrotron Radiation (IPS), 76344 Eggenstein-Leopoldshafen, Germany

^e Applied Chemistry and Engineering Research Centre of Excellence (ACER CoE), Université Mohammed VI Polytechnique (UM6P), Lot 660, Hay Moulay Rachid, Ben Guerir 43150, Morocco

^f Instituto de Investigaciones en Fisicoquímica de Córdoba, INFIQC-CONICET, Av. Haya de la Torre esq. Medina Allende, Ciudad Universitaria, 5000, Córdoba, Argentina

^g Departamento de Química Teórica y Computacional, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, Argentina

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ABSTRACT

Lithium-rich manganese spinels have attracted sustained interest because they promise high lithium-ion-sieve capacity. Although the material with nominal composition $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ presents better performance than those belonging to the $\text{Li}_{(1+\delta)}\text{Mn}_{(2-\delta)}\text{O}_4$ series, yet its exact crystal chemistry and structure remains controversial. In the present experimental and theoretical study, the material was synthesized by spray-drying followed by calcination, obtaining the target stoichiometry in which Mn is present with the 4+ oxidation state.

Rietveld refinements were performed to synchrotron X-Ray diffraction patterns using Full Prof and FAULTS programs to model stacking-fault-induced reflections broadening. The refinement revealed a two-phase system, formed by ~80 wt% of cubic spinel $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ and ~20 wt% of monoclinic-layered Li_2MnO_3 , together reproducing the overall $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ composition. ^7Li solid-state NMR confirmed that lithium occupies 8a and 16d sites in the spinel and the presence of the Li_2MnO_3 phase. Furthermore, density functional theory calculations revealed that a slight stoichiometric imbalance in the Li/Mn ratio around 1 in $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ could lead to metastable spinel phases, with Li_2MnO_3 as main secondary product.

1. Introduction

As one of the key elements for the energy transition, lithium has become an increasingly central element in net zero carbon technologies. In 2023, global annual production of lithium raw materials, from hard rock, brines and clays, reached approximately 190,000 tons of lithium, including 70,000 tons from brine sources and 120,000 tons from hard rock deposits [1]. This represents a more than twofold increase in lithium production over the past three years [1]. It plays a central role especially in the manufacturing of lithium-ion batteries used in automotive and stationary energy storage. Currently, lithium mining in Europe is limited as its share of global production is less than 0.4% in 2020 [2].

Today lithium is mainly extracted from hard rocks in Australia and China via acid roasting process as well as from Salars in South America via solar evaporation. Acid roasting is highly energy-intensive and requires large amounts of acid for its operation [3]. In the solar evaporation process the Li-recovery rate is low and the process requires much time making it inefficient [2]. In order to develop a more environmentally friendly process for the Li-extraction and to meet growing demand of the metal, novel extraction processes are developed to enable Li-extraction from alternative resources. In this context, Direct Lithium Extraction (DLE) is of particular importance as it allows rapid lithium recovery with minimal land requirements and high lithium recovery rates [4]. Lithium extraction technologies include solvent extraction [5], precipitation [5], membrane separation [6], and sorption processes [4];

* Corresponding authors at: Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), 76344 Eggenstein-Leopoldshafen, Germany.

E-mail addresses: martina.gamba@cetmic.unlp.edu.ar (M. Gamba), fabian.jeschull@kit.edu (F. Jeschull).

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among these, sorption processes are considered particularly promising. This sorption-process can be divided into two mechanisms- First, adsorption processes where lithium ions are physically or chemically bound to the surface of a material (LDH). Second, ion-exchange processes where lithium ions replace another ionic species (mostly protons) in the host structure of the sorbent material. In this regard Lithium Manganese Oxides (LMOs) and Lithium Titanium Oxides (LTOs) are discussed. Due to their rapid kinetics, high adsorption capacity and high selectivity, LMOs are particularly promising candidates [7]. A significant limitation in the synthesis of LMOs lies in limited potential for scale-up. In [8] a novel spray drying process was presented to synthesize LMOs in a continuous flow process enabling scalability of the sorbent production. Based on diffraction and electron microscopy data, the material comprised of an impurity phase, ascribed to Li_2MnO_3 , that dissolved in the activation step with hydrochloric acid solution.

Establishing a detailed structural baseline of this as-prepared material is a critical prerequisite that not only dictates the mechanistic pathways of the activation process itself, but also provides a necessary framework for accurately comparing diverse literature reports regarding maximum lithium uptake, chemical stability, and ion exchange kinetics. Our initial findings have motivated an in-depth analysis of the as-prepared LMO using a complementary suite of analytical tools, including solid-state nuclear magnetic resonance (^7Li MAS NMR) and synchrotron-based X-ray absorption spectroscopy (XAS), as well as high-resolution in-house and synchrotron-based X-ray diffraction (XRD) data. Combined with density functional theory calculations (DFT), this approach led to a revised structural model based on a multiphase system that harmonizes earlier interpretations. Ultimately, rather than assigning the nominal composition of $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ to a single-phase structure, our analysis refines this perspective to a two-phase material description comprising the well-known lithium manganese oxides, Li_2MnO_3 and $\text{Li}_4\text{Mn}_5\text{O}_{12}$.

2. Background

Among lithium–manganese oxides, particular attention has been devoted to the compound with nominal formula $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ first reported by Chitrakar et al. [9]. This is the first article in which the new phase derived from the thermal oxidation of orthorhombic LiMnO_2 was introduced. It was explicitly presented as a material that lies outside the conventional Li–Mn–O phase diagram. At the time, lithium-rich spinel compositions were generally limited to $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$, which was considered the upper boundary of lithium excess in stable spinel-type phases with Mn oxidation state 4+. The composition $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ therefore represented a significant extension beyond this limit. The motivation for synthesizing such a lithium-rich compound was directly linked to its application as a lithium ion-sieve precursor: a higher initial lithium content was expected to yield an ion-sieve structure with increased lithium uptake capacity. The material was firstly synthesized by heating at 400 °C the precursor LiMnO_2 promoting the oxidation of Mn^{3+} to Mn^{4+} , leading to the formation of a single-phase material rather than a mixture of LiMn_2O_4 and Li_2MnO_3 , as commonly reported. This behavior was attributed to the small crystallite size of the precursor and improved oxygen contact, enabling complete oxidation. The obtained X-ray diffraction (XRD) pattern was indexed to a face-centered cubic lattice with a parameter of 8.14 Å, suggesting a spinel-related structure [9].

A central issue is that the composition $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ does not satisfy the ideal 3:4 cation-to-anion ratio of a normal cubic spinel, implying the presence of defects such as oxygen vacancies, interstitial cations, or cation vacancies. Three structural models were examined by the authors in further articles: a rhombohedral layered model with cation deficiency ($\text{R}\bar{3}\text{m}$), an oxygen-deficient spinel and a model with lithium on interstitial 16c site. In a first approach, the authors suggested that the layered model better accounted for the reflection's intensity distribution, leading to the proposal that the structure originates from a disordered rock-salt-type arrangement derived from the LiMnO_2 precursor [9]. In a

second approach, the authors stated that from Rietveld and TEM analyses (results not published) the material was a lithium-rich and defective spinel with oxygen vacancies, within the cubic $\text{Fd}\bar{3}\text{m}$ space group [10]. In this model, lithium would occupy the tetrahedral 8a site as in a normal spinel, but a significant fraction of lithium would also substitute manganese in the octahedral 16d site. The composition was expressed as $(\text{Li})_{8a}[\text{Li}_{0.5}\text{Mn}_{1.5}]_{16d}\text{O}_{3.75}$ indicating both cation disorder and oxygen deficiency. This approach abandoned the explicit layered description suggested before, and instead explained the non-stoichiometry through lithium incorporation into octahedral positions and the presence of oxygen vacancies. In a third article, the authors suggested a new model based on unpublished neutron powder diffraction data in which the cation distribution in $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ was described as $(\text{Li}_{0.68} \times 0.32)_{8a}[\text{Li}_{0.4}\text{Mn}_{1.6}]_{16d}[\text{Li}_{0.52}]_{16c}\text{O}_4$ (where X = vacancies) [11]. In this model, lithium ions partially occupy the 8a site, leaving 32% of these sites vacant, while lithium and manganese fully occupy the 16d site and the remaining lithium ions are located at octahedral 16c site.

More recently, Gao et al. [12], consolidated the earlier interpretations of the presence of interstitial sites or vacancies in the model, by explicitly proposing two preferred structural models within the cubic spinel framework: $(\text{Li})_{8a}[\text{Li}_{0.4}\text{Mn}_{1.6}]_{16d}[\text{Li}_{0.2}]_{16c}\text{O}_4$ and $(\text{Li})_{8a}[\text{Li}_{0.5}\text{Mn}_{1.5}]_{16d}\text{O}_{3.75}$. In both descriptions, the structure was based on a cubic close-packed oxygen lattice, with Mn^{4+} primarily occupying octahedral 16d site, while lithium occupies not only the normal tetrahedral 8a site but also partially the octahedral 16d site, and in the first model additionally the interstitial 16c site. The first model emphasizes the presence of interstitial lithium, whereas the second highlights oxygen deficiency as the compensating mechanism. In that sense, the authors [12] unify the earlier competing hypotheses by showing that both interstitial lithium and oxygen vacancies are viable and closely related descriptions of the same defective spinel framework.

Despite these unifying efforts, the precise lithium distribution and phase composition of materials with nominal stoichiometry $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ remain a subject of active investigation. While standard X-ray diffraction serves as an invaluable tool for general phase identification, relying predominantly on comparative diffraction patterns makes it challenging to fully resolve the subtle structural nuances of closely related secondary phases inherent to LMO derivatives. As highlighted earlier, establishing a structural baseline of the as-prepared material is essential for making fair, accurate comparisons regarding the lithium extraction capabilities reported across the literature. To resolve these structural ambiguities, we integrate ^7Li MAS NMR and atomistic modelling (DFT) alongside X-ray diffraction, capturing structural features across different length scales.

3. Materials and methods

3.1. Preparation of the material

A material with nominal composition $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ (LMO) was synthesized in a spray drying process according to Herrmann et al. 2025. Lithium acetate solution was prepared mixing 109.17 g (1.07 mol) lithium acetate dihydrate ($\text{Li}(\text{CH}_3\text{COO}) \cdot 2\text{H}_2\text{O}$, Purity 98%, Acros Organics) with 0.4 l deionized water. Manganese acetate solution was prepared by adding 262.25 g (1.07 mol) manganese (II) acetate tetrahydrate ($\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, Purity >99%, Sigma Aldrich) in 0.8 l of deionized water. These solutions were mixed and processed in a spray-dryer (GEA Niro MOBIL MINOR). The inlet and outlet temperatures of the carrier gas (N_2) were $T_{\text{Inlet}} = 210$ °C and $T_{\text{Outlet}} = 112$ °C. A coarse fraction of 75.8 g and a fine fraction of 155.5 g were obtained from the spray dryer. The powder was mixed again for further synthesis. Subsequently the Li-Mn-salt was calcined at 450 °C for 5 h.

3.2. Chemical analysis

The Li and Mn contents of the solid was measured by inductively

coupled plasma optical emission spectroscopy (ICP-OES, 700 Series: Agilent Technologies). The material was digested using 37 wt% HCl solution and H₂O₂. The composition of the solution was determined using ICP-OES, and from this, the Li/Mn ratio of the material and the overall molecular formula was calculated (Table 2).

3.3. XAS

The X-ray absorption spectra (XAS) were recorded at the XAS beamline of the KIT Light Source in Karlsruhe, Germany. Powders were pressed into dense pellets, loaded into a sealed transfer device, and moved to the beamline without exposure to air. Once the samples were in place, the pressure in the experimental chamber was lowered to below 0.1 mbar to suppress beam-induced alterations, air-related fluctuations, and atmospheric absorption. For the ionisation chambers the gas composition was tuned to obtain 15% absorption in the first chamber, 30% in the second and 60% in the third at 7 keV, which covers all edges of interest. Helium served as the flushing gas, while nitrogen and argon were mixed in the chambers (IC Spec, XDS Oxford) to achieve the desired attenuation. The third chamber also housed a metal foil reference, allowing continuous energy calibration of the beamline and on-the-fly recalibration of the spectra when required.

Fluorescence detection employed a Vortex-90EX silicon-drift detector (Hitachi High-Tech USA) mounted through a double-O-ring vacuum feed-through, positioned 5 cm from the centre of the sample. Data were collected in step mode with the following energy-step scheme: –150 eV to –50 eV before the edge (5 eV steps), –50 eV to the edge (1 eV steps), the edge region from –20 to +20 eV (0.5 eV steps), and finally the EXAFS region up to $k = 16 \text{ \AA}^{-1}$ (0.05 k steps, with the k-range continuously extended by 0.5 k during acquisition).

Because the transmission signal provided a superior signal-to-noise ratio, all subsequent XANES and EXAFS analyses were performed on the transmitted data. Spectra were extracted using a custom IgorPro (Wavemetrics) routine based on the EXAFS123 library from Scarrow [13]. Unlike many EXAFS packages, this code does not adjust the background spline until the low-R contribution $X(R)$ is minimized, ensuring a stable background. Edge positioning is handled automatically, and the background-plus-edge model combines a sigmoidal function with several peaks and a cubic spline, yielding highly reproducible XANES spectra without user intervention.

3.4. X-Ray measurements and structural refinements

Powder X-ray diffraction (XRD). Diffraction experiments on LMO were performed using lab diffractometers with transmission geometry: (i) a STOE STADI-P double-sided setup with the Mo K α 1 radiation ($\lambda = 0.70932 \text{ \AA}$), Ge(111) monochromator, and linear MYTHEN2 detector, with detector operated in stationary mode centred at 18° , covering a 2θ range approximately from 5° to 45° , with an angular resolution of 0.015° and total exposure time of 60 min; (ii) a STOE STADI-MP in Theta/2Theta mode with Cu K α 1 radiation ($\lambda = 1.540562 \text{ \AA}$), Ge(111) monochromator, and linear MYTHEN1 detector with 0.015° angular resolution. The detector was moved in steps of 0.5° covering a 2θ range from 10° to 80° . Total exposure time was varied from 30 min to 4 h. Prior to scanning, powdered samples were placed between round adhesive Kapton foils and mounted in a STOE transmission sample holder.

In addition, Synchrotron X-Ray diffraction was conducted at the P02.1 beamline of the PETRA III synchrotron (DESY, Hamburg, Germany). A monochromatic X-ray beam with a photon energy of approximately 60 keV was employed ($\lambda = 0.207337 \text{ \AA}$). A Varex XRD 4343CT detector, featuring a $150 \times 150 \mu\text{m}^2$ pixel size and a total resolution of 2880×2880 pixels was used. The detector utilizes a CsI scintillator directly deposited on amorphous silicon photodiodes. The sample-to-detector distance was maintained at approximately 1500 mm. Samples were prepared in 0.5 mm diameter glass capillaries. A typical measuring time of approximately 60 s per capillary was applied. LaB₆ was used as a

reference standard for calibration. Calibration was performed using the DAWN2 software, with subsequent 2D-to-1D conversion (vs. 2 θ) carried out via DAWN2 and custom Python scripts.

Structural Refinement. Initial phase identification was carried out with Match! Software. Fullprof suite was used for Rietveld refinements to the synchrotron XRD data. Profile function no. 7, a Thompson-Cox-Hastings pseudo-Voigt function convoluted with an axial divergence asymmetry function, was used for modelling. Instrumental resolution parameters (U, V, W) were extracted from Instrumental Resolution File obtained from LaB₆ standard refinement. The individual thermal displacement factors for the different crystallographic sites (B_{iso}) have been fixed to the values listed in the data sets. We explicitly decided not to refine B_{iso} of each element, because its refinement would lead to a strong correlation with occupancies [94]. Instead, fixed values of B_{iso} from neutron diffraction data [95] were used and, in addition, introduced a refinable overall thermal displacement factor (B_{ov}) that also allowed negative values. The sum of B_{ov} and B_{iso} yields an effective isotropic displacement parameter that remains positive for all sites. B_{ov} is strongly correlated to the scale factor (as seen in the correlation matrix), and can be interpreted as an empiric value that compensates for intensity mismatches mostly at higher 2θ values, due to setup-related polarization effects. Further, cationic form factors for Mn⁴⁺ and O²⁻ have been utilized in this work (and not form factors for the neutral atoms). During refinement, zero shift, scale factors and background points were first refined. Then, lattice parameters, U and X (related to strain), Y (related to crystallite size) and B_{ov} were allowed to vary. Only for the main phase, atomic positions and occupancy factors were refined (when indicated). The standard deviations given in brackets after the refined parameters are the standard deviations obtained by the Rietveld refinement multiplied by a specific factor according to [14].

The FAULTS program [15] was employed to model the stacking-fault-disordered layered phase observed in the diffractogram of pristine LMO. Representations and analyses of the crystal structures were done using the program VESTA [16].

3.5. ⁷Li MAS NMR spectroscopy

⁷Li magic-angle spinning nuclear magnetic resonance (⁷Li MAS NMR) spectroscopy was performed at a magnetic field of 4.7 T, corresponding to a resonance frequency of 77.8 MHz. Spinning was performed in 1.3 mm rotors at 55 kHz. Spectra were acquired with a rotor-synchronized Hahn-echo pulse sequence and a $\pi/2$ pulse duration of 0.85 μs . The recycle delay was 1 s, well above five times the T1 relaxation time.

Spectra were referenced to an aqueous solution of 1 M LiCl at 0 ppm and normalized with respect to sample mass and number of scans. The area fractions of the NMR peaks were converted to weight fractions (as obtained from the XRD refinement) via the molar masses and the number of Li per formula unit.

3.6. DFT Methodology and modelling

DFT-based simulations were carried out using the Siesta software. These were run under the Kohn–Sham scheme, employing norm-conserving pseudopotentials and the GGA-PBE exchange-correlation functional. Spin polarization and long-range dispersion corrections were included via the DFT-D3 method [17,18]. To properly account for strong electronic correlations in Mn transition metal cations, the GGA + U method was used with $U = 3.9 \text{ eV}$ [19]. The geometry was optimized under variable cell condition using the conjugate gradient method. The convergence criterion for energy and forces was 10^{-4} eV and $0.02 \text{ eV \AA}^{-1}$. A $3 \times 3 \times 3$ Monkhorst-Pack mesh in the Brillouin zone (BZ) was used for geometry optimization and $6 \times 6 \times 6$ for density of states calculations. The free energies for the chemical transformations were obtained under the ΔE_{DFT} approximation using the formation energies (E_{f}) of each species as references.

3.6.1. Description of spinel series

With the aim of understanding the cationic distribution in the material with nominal composition $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$, a series of cubic lithium–manganese related oxides with different Li/Mn ratio were used in the computational studies. Their representation is described below, and summarized in Table 1.

LiMn_2O_4 . The conventional cubic $Fd\text{-}3m$ LiMn_2O_4 spinel structure involving the $(\text{Li}_8)_8\text{a}[\text{Mn}_{16}]_{16d}\text{O}_{32}$ atomic distribution per unit cell was used as starting point [20]. In this composition, Mn is present with oxidation state 3.5 +.

$\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$. This composition belongs to the series $\text{Li}_{(1+\delta)}\text{Mn}_{(2-\delta)}\text{O}_4$ ($\delta = 0.33$). However, to represent it, building a $5 \times 1 \times 1$ supercell is necessary, which increases drastically the computational time and loses the cubic symmetry of the cell, introducing anisotropies. Instead, a close composition of $\text{Li}_{1.25}\text{Mn}_{1.75}\text{O}_4$ was studied by replacing Mn in the 16d site with Li, using the conventional cubic spinel atomic distribution previously described (Table 1). In this composition and further ones, Mn has an average oxidation state of 4 +.

$\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$. This composition does not belong to the series $\text{Li}_{(1+\delta)}\text{Mn}_{(2-\delta)}\text{O}_4$, and necessarily, vacancies and/or new interstitial sites must be added in the representations to achieve it. First, the distribution $(\text{Li}_8)_8\text{a}[\text{Li}_{0.4}\text{Mn}_{1.6}]_{16d}[\text{Li}_{0.2}]_{16c}\text{O}_4$ was considered. However, it is unattainable as the previously mentioned representations without losing the cubic symmetry of the supercell and increasing drastically the computing time. Following, using the conventional spinel representation $(\text{Li}_8)_8\text{a}[\text{Mn}_{16}]_{16d}\text{O}_{32}$ the desired composition was achieved by replacing three Mn atoms in 16d positions with Li, while adding two Li in 16c site. This led to the atomic distribution $(\text{Li}_8)_8\text{a}[\text{Li}_3\text{Mn}_{13}]_{16d}[\text{Li}_2]_{16c}\text{O}_{32}$, which corresponds to the final stoichiometry $\text{Li}_{1.625}\text{Mn}_{1.625}\text{O}_4$. In the same representation, the near atomic distributions $(\text{Li}_8)_8\text{a}[\text{Li}_2\text{Mn}_{14}]_{16d}[\text{Li}_3]_{16c}\text{O}_{32}$ and $(\text{Li}_8)_8\text{a}[\text{Li}_3\text{Mn}_{13}]_{16d}[\text{Li}_3]_{16c}\text{O}_{32}$ were also studied to evaluate the effect of excess of Li in the 16c site and the effect of varying the Li/Mn ratio around 1 (Table 1). These structures were built based on the optimized $\text{Li}_{1.25}\text{Mn}_{1.75}\text{O}_4$.

To generate an ordered structural model, one Li atom was initially placed at the crystallographic 16c position (0,0,0), while the second Li atom can be placed at different crystallographic 16c position. The Li 16c atom at (0,0,0), and ordered distribution of Li at 16d sites breaks the ideal symmetry. In consequence the different 16c sites are no longer energetically equivalent. To determine the energy of the sites, the non-equivalent initial configurations were optimized and the lowest-energy relaxed structure among those was selected (see Appendix C, Table C1). It is important to note that the simultaneous occupation of the crystallographic 8a and 16c sites in the initial model involves unrealistically short Li–Li separations (~ 1.8 Å). However, during the structural relaxation this Li–Li distance increased up to 2.38 Å through local rearrangements of the Li sublattice. These rearrangements are accompanied by a reorganization of the local Li coordination polyhedral, while preserving the Mn–O framework and the overall spinel-like structure, producing only minor changes in the lattice parameters and unit-cell volume. However, the lowest-energy configuration is characterized by the transformation of a Li atom initially located in a tetrahedral environment (8a), into an octahedral coordination environment after relaxation. In contrast, higher-energy configurations

Table 1
Compositions evaluated in DFT and their atomic distributions.

Formula	Representation And atomic distribution	Li/Mn ratio	δ^a
LiMn_2O_4	$(\text{Li}_8)_8\text{a}[\text{Mn}_{16}]_{16d}\text{O}_{32}$	0.5	0
$\text{Li}_{1.25}\text{Mn}_{1.75}\text{O}_4$	$(\text{Li}_8)_8\text{a}[\text{Li}_2\text{Mn}_{14}]_{16d}\text{O}_{32}$	0.75	0.25
$\text{Li}_{1.625}\text{Mn}_{1.75}\text{O}_4$	$(\text{Li}_8)_8\text{a}[\text{Li}_2\text{Mn}_{14}]_{16d}[\text{Li}_3]_{16c}\text{O}_{32}$	0.93	–
$\text{Li}_{1.625}\text{Mn}_{1.625}\text{O}_4$	$(\text{Li}_8)_8\text{a}[\text{Li}_3\text{Mn}_{13}]_{16d}[\text{Li}_2]_{16c}\text{O}_{32}$	1	–
$\text{Li}_{1.5}\text{Mn}_{1.5}\text{O}_{3.75}$	$(\text{Li}_8)_8\text{a}[\text{Li}_4\text{Mn}_{12}]_{16d}\text{O}_{30}$	1	–
$\text{Li}_{1.75}\text{Mn}_{1.625}\text{O}_4$	$(\text{Li}_8)_8\text{a}[\text{Li}_3\text{Mn}_{13}]_{16d}[\text{Li}_3]_{16c}\text{O}_{32}$	1.08	–

^a Corresponds to the Li excess in the general composition $\text{Li}_{(1+\delta)}\text{Mn}_{(2-\delta)}\text{O}_4$.
“–” indicates that the formula do not belong to the series $\text{Li}_{(1+\delta)}\text{Mn}_{(2-\delta)}\text{O}_4$

converge to alternative local coordination geometries, including highly distorted or square-pyramidal-like coordination, indicating that the local Li environment has a significant influence on the relative stability of the structures (Appendix C, Figs. C1–3).

A second model, based on vacancies was also considered, as suggested in literature (Table 3). The $\text{Li}_{1.5}\text{Mn}_{1.5}\text{O}_{3.75}$ composition can be reached from the $(\text{Li}_8)_8\text{a}[\text{Mn}_{16}]_{16d}\text{O}_{32}$ representation by replacing four Mn with Li at the 16d site and by removing two oxygen atoms from the unit cell yielding in $(\text{Li}_8)_8\text{a}[\text{Li}_4\text{Mn}_{12}]_{16d}\text{O}_{32}$. It is important to note that the Li atoms in the 16d site induce a local charge imbalance, increasing the charge density on the O atoms that are bonded to Mn and Li in 16d site. This makes them more susceptible to generating vacancies. Thus, two oxygen atoms separated by 8 Å from each other within the Mn–Li octahedra (16d) which were connected by a vertex, were removed. Then, the structure was optimized.

3.7. Literature screening and classification

A literature search was performed using the Scopus database for studies published between 1998 and March 2026, using “ $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ ” as search term. The resulting publications were screened for studies reporting X-ray diffraction data for the $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$, the precursor of the actual ion-sieve obtained through its delithiation, $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$. Publications that did not provide an XRD-based structural assignment of the investigated material were excluded. A total of 73 articles were found which match this criterion and further analyzed.

For classification, only the interpretation explicitly stated by the authors in the text, figure captions, or ICDD/PDF reference card numbers indicated in the diffractograms were considered. Only what was explicitly written by the authors concerning the XRD patterns and the assignment or not to the ICDD/PDF 52–1841 entry in the text or in the Figure, was taken into account. Based on the reported interpretations of the XRD patterns, three main lines were found and the articles were categorized accordingly: (i) the authors assigned the XRD reflexes exclusively to $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$, ICDD/PDF 52–1841, a cubic $Fd\text{-}3m$ structure, or a spinel structure, without reporting an additional crystalline phase; (ii) spinel and Li_2MnO_3 phases were explicitly identified; and (iii) the authors explicitly reported spinel + unassigned reflections, when additional diffraction reflections were identified but were not assign to a crystalline phase.

The number of studies assigned to each category was divided by the total number of studies fulfilling the inclusion criteria to obtain the percentages reported in Table 3.

4. Results and discussion

4.1. Structural analysis of LMO

In literature there are various compositions of lithium manganese oxides with general formula $\text{Li}_x\text{Mn}_y\text{O}_4$ and Li/Mn ratio range of $0.5 < \frac{x}{y} < 1$. The targeted composition in the present work was $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ ($\frac{x}{y} = 1$). It was synthesized by a two-step solid-state synthesis method: a precursor was prepared by spray-drying for homogenous mixing of the corresponding acetate salts, followed by calcination. The resulting powder which was labelled as LMO was characterized by ICP and XAS to

Table 2
Characteristic of LMO with nominal composition $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$. The Li/Mn ratio was determined by ICP-OES measurements and the Mn oxidation state by synchrotron based XAS.

Name of the sample	Li/Mn ratio ^a	Ox. State of Mn ^b
LMO (“ $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ ”)	1.01	+4.0

^a Obtained from ICP-OES measurements.

^b obtained from XAS measurements

determine its chemical composition and oxidation state of Mn, respectively, as summarized in Table 2. As it can be seen, the oxidation state of Mn in LMO is 4+, and the Li/Mn ratio matches well with the expected stoichiometry. XAS curves can be seen in the Appendix A, Fig. A1.

Influence of X-ray source energy on phase identification. X-ray-diffraction patterns of LMO obtained with lab diffractometers with Cu K α and Mo K α radiation are shown in Fig. 1a and b, respectively. As it is expected, the usage of a less energetic X-ray (Cu K α , Fig. 1a), reduced the signal to noise ratio when compared to Mo K α (Fig. 1b). While a standard 1 h experiment with the Mo source clearly shows a reflection at $2\theta = 9.5^\circ$ ($d = 4.3 \text{ \AA}$), the same reflection when using Cu source ($2\theta = 20.8^\circ$) disappeared into the background at a comparable exposure time (30 min – 1 h), therefore requiring much longer acquisition times (2–4 h) to achieve similar information. This is known to happen due to the combination of fluorescence and absorption phenomena: Cu K α radiation (8.05 keV) excites Mn K fluorescence (Mn K edge = 6.539 keV), raising the background and lowering the peak-to-background ratio. In addition, lithium-manganese oxides also exhibit a high mass-attenuation coefficient. For example, Li_2MnO_3 at 8.05 keV has a mass-attenuation coefficient of $129.9 \text{ cm}^2 \text{ g}^{-1}$ for a packing fraction of 0.6 and a sample thickness of 0.4 mm while at higher energies (for example, for Mo K α radiation 17.5 keV) the value turns to be $15.46 \text{ cm}^2 \text{ g}^{-1}$ [21].

When doing the phases identification analysis, it is observed that the strongest reflections can be interpreted either on the basis of the reference pattern commonly used in the literature for the nominal composition $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ (ICDD 52–1841), or on the basis of the reference pattern corresponding to the cubic spinel $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ (ICDD 01–080-2978, space group Fd-3m) (Fig. 1b). It is not possible, based solely on the relative intensities and positions of the reflections, to distinguish between the two cards. An even more important point is that neither of them can account for the signal present at $2\theta = 9.5^\circ$ and $2\theta = 20.8^\circ$ in Mo and Cu diffraction patterns, respectively. Instead, this reflection was unequivocally assigned to the monoclinic layered Li_2MnO_3 phase (ICDD

01–085-6632, space group C2/m), whose principal reflections strongly overlap with those of the spinel (Fig. 1b). The superstructure reflections associated with Li_2MnO_3 are weakly developed, the 020 reflection being the most intense among them. Its asymmetric Warren-type line shape, characterized by a gently sloping right-hand tail, originates from stacking faults along the c-axis.

The formation of the layered Li_2MnO_3 phase was further validated in a second LMO sample (identical Li/Mn ratio = 1 and Mn oxidation state = 4+) prepared following a previously reported hydrothermal method [9,22,23]. In Appendix A, the conditions used for the synthesis, ICP-OES results and X-Ray diffraction patterns are shown. Our results confirm a mixed phase system comprising of a cubic spinel $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ and a monoclinic layered Li rich phase Li_2MnO_3 , both with oxidation state 4+.

Assuming a molar fraction n of Li_2MnO_3 and $(1 - n)$ of $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$, the overall Li/Mn ratio can be expressed mathematically as:

$$\frac{2n + 1.33(1 - n)}{n + 1.67(1 - n)} = 1 \quad (1)$$

Solving Eq. 1, yields $n \approx 0.25$, i.e., 25% mol Li_2MnO_3 and 75% mol $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$. In mass terms this corresponds to $\approx 19\%$ Li_2MnO_3 and $\approx 81\%$ $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$. Because each end-member satisfies charge neutrality with Mn in the 4+ oxidation state ($2 \text{ Li}^+ + \text{Mn}^{4+} + 3 \text{ O}^{2-} = 0$ and $1.33 \text{ Li}^+ + 1.67 \text{ Mn}^{4+} + 4 \text{ O}^{2-} = 0$), the combined system retains an average Mn oxidation state of 4+ while the overall Li/Mn ratio equals 1.

Nuclear Magnetic Resonance Spectroscopy. To further confirm the presence of different crystallographic phases in LMO, ^7Li MAS NMR spectroscopy was performed. The spectrum in Fig. 2 shows a dominant contribution at 710 ppm with a shoulder toward higher chemical shifts, suggesting at least two different crystallographic sites. Deconvolution yields a narrow peak at 714 ppm, which can be assigned to the 4 h site in

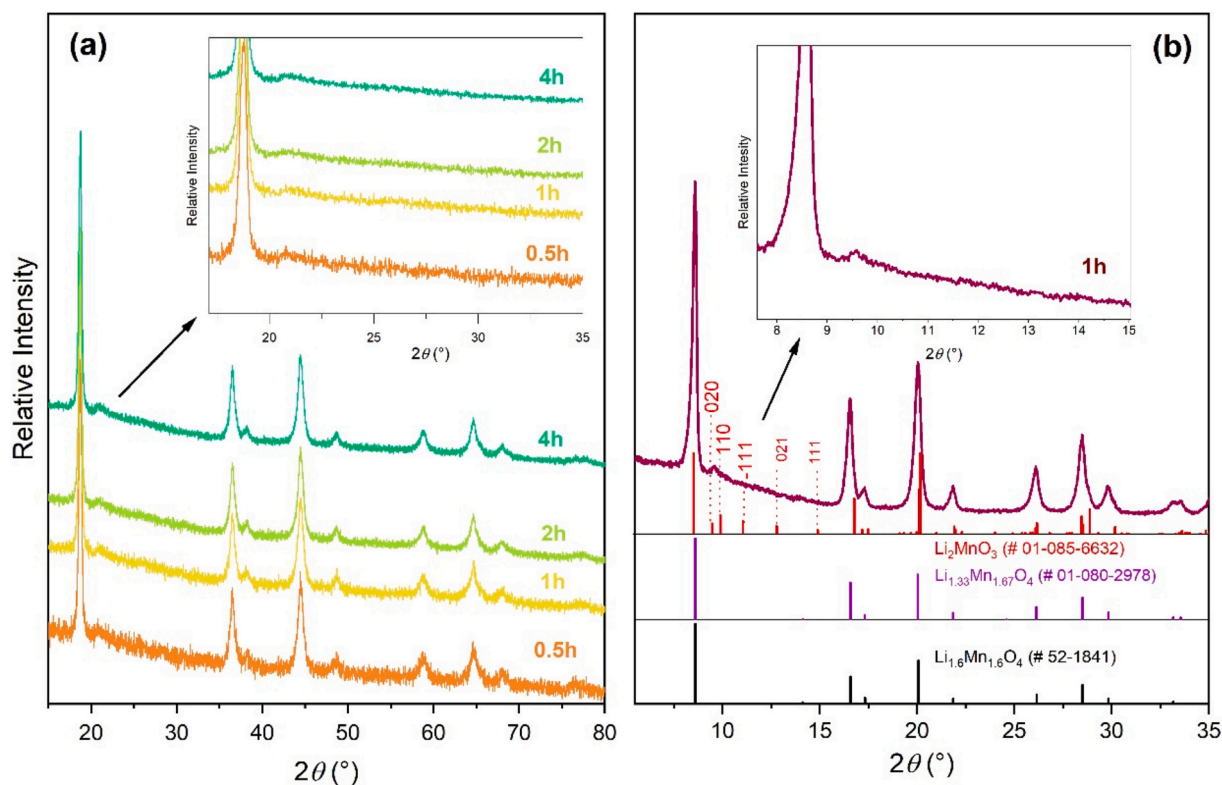


Fig. 1. Diffractogram of LMO ($\text{Li}_x\text{Mn}_y\text{O}_4$ with $\frac{x}{y} = 1$ and Mn oxidation state = 4+), obtained with Cu-K α (a) and Mo-K α (b). Exposure time of measurements is indicated in the Graphs.

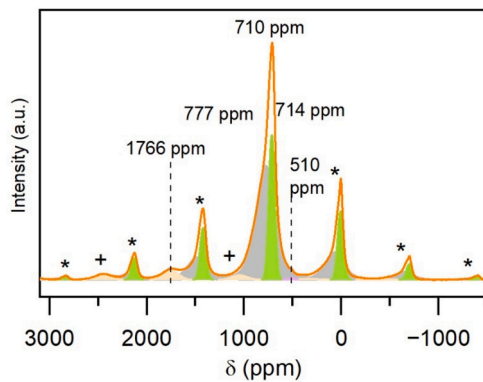


Fig. 2. ^7Li MAS NMR spectrum of LMO ($\text{Li}_x\text{Mn}_y\text{O}_4$ with $\frac{x}{y} = 1$ and Mn oxidation state = 4+). Spinning sidebands are marked with asterisks and plus signs.

layered Li_2MnO_3 [24–26]. This phase was also identified via the superstructure reflections in the XRD pattern described above. In addition, a broader feature at 777 ppm can be assigned to the tetrahedral 8a site in $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ spinel. The area fractions of these two peaks are 29.5% and 64.8%, respectively. A notable feature at 1766 ppm can be assigned to the octahedral 16d site $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ spinel phase (accounting for an area fraction of 5.5%) [25]. Overall, the 30:70 ($\text{Li}_2\text{MnO}_3/\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$) area fraction is in good agreement with the XRD phase analysis described above. The very weak peak at 510 ppm corresponds to a minute amount (<1%) of LiMn_2O_4 [25,27] in agreement with decomposition products indicated by DFT calculations (see below). The layered Li_2MnO_3 phase should also show another peak at about 1450 ppm [25,26], which in this case is superimposed with other spinning sidebands rendering a more detailed quantification of the site occupancies challenging.

In summary, the ^7Li MAS NMR spectrum can be well described with four different contributions that are reported in earlier publications and we assign these peaks accordingly to the different crystallographic sites in the multiple phases. Due to the strong overlapping of the isotropic peaks and the spinning sidebands, we cannot fully exclude the presence of additional structural features as minor contributions in the overall signal.

Structural Models Reported in Literature. Based on 73 studies found between 1998 and March 2026 at the Scopus data base using the formula $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ as the search term, and which provided XRD data, three main lines of interpretation of the XRD patterns for materials with this nominal composition were found (Table 3):

- (1) 86.3% of the revised articles assign the XRD reflexes exclusively to the spinel phase without mentioning any other additional reflexes or phases. In this group we included those articles which explicitly mention a cubic/spinel phase, the space group Fd-3m , and/or the reference to the ICDD/PDF entry 52–1841, corresponding to “ $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ ”, either in the text, figures or figures caption;

Table 3

Review of bibliography reporting XRD patterns of the material with nominal composition $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ (Scopus search on “ $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ ”, including XRD studies between 1998 and 2026).

#	Assignment	References	%
1	Cubic/spinel phase without reporting any additional crystalline phase	[9–12,22,28–85]	86.3
2	Cubic/spinel + monoclinic Li_2MnO_3 as secondary phase	[8,86–93]	12.3
3	Cubic/spinel + not assigned extra reflections	23	1.4

- (2) 12.3% explicitly reported Li_2MnO_3 (C2/m) in addition to the main spinel phase;
- (3) 1.4% explicitly acknowledged additional diffraction reflections that remained unassigned. Importantly, these statistics describe how the XRD patterns were interpreted in the original publications.

Our own interpretation of the published diffractograms based on our structural reassessment of the $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ system, indicates that the presence of a Li_2MnO_3 secondary phase had been overlooked in a large number of studies reporting nominal $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ as a single cubic spinel phase.

This could have happened due to a combination of several factors: i) the Li_2MnO_3 phase fraction would account for less than 20% wt (Eq. 1), ii) as explained before, its main reflections overlap with the main reflection of the cubic spinel phase and the weak reflections tend to broaden due to the development of stacking faults, iii) Cu $\text{K}\alpha$ X-Ray absorbance and fluorescence processes, when instrumentation and experimental settings are not optimized, make the reflections of the secondary phase to fall under the background. All these factors together, in addition to size effects could make the Li_2MnO_3 superstructure reflections often appear as “missing” in routine Cu-XRD patterns. This is particularly relevant in the light of the widely cited reference data ICDD 52–1841, which originated from an initial report by [9] and relied exclusively on Cu $\text{K}\alpha$ radiation for its characterization. The structural reference became the principal reference for phase assignment of subsequent diffractograms in literature in the field of direct lithium extraction.

We postulate herein that these are reasons that contributed as to why materials with the nominal stoichiometry $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ were believed to be a single-phase system. The formation of the Li_2MnO_3 impurity phase could thus be the result of the lithium excess used in the synthesis, thus raising the question if the reported syntheses and material design strategies should be revisited. For instance, group 2 contains examples that propose Li_2MnO_3 acid-resistant surface coating. The Li_2MnO_3 phase fraction may play a role in the material properties of the resulting HMO after the activation step of LMO in strongly acidic environments. This leaves the remaining absorber phase with a higher surface area and porosity after the dissolution of Li_2MnO_3 .

Development of a New Structural Model. LMO was characterized using synchrotron X-ray diffraction, where the high beam brilliance enabled the sensitive detection of subtle secondary phases. The resulting diffraction patterns displayed significantly improved peak definition, allowing for a more reliable analysis of the structural features. Rietveld refinements of the pattern was conducted, using Fullprof suite (Fig. 3). In the following, we gradually develop a new structural model for the lithium manganese oxide with nominal composition $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$, as outlined in Table 4. Models 1 and 2 use single-phase structural models based on the atomic distribution suggested previously in literature (and summarized in Section 2). In Models 3 to 5, a secondary phase was introduced, to acknowledge for features that remained unexplained using the former models. The detailed refinement process is described in section 3.4.

Model 1 & 2 – Highlighting the Issues with Single Phase Structural Models. At an initial stage, two single phase models based on $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ cubic phase (ICDD 1514017, space group = Fd-3m , N° 227) were evaluated (Table 4): (1) $(\text{Li})_{8a}[\text{Li}_{0.4}\text{Mn}_{1.6}]_{16d}[\text{Li}_{0.2}]_{16c}\text{O}_4$ and (2) $(\text{Li})_{8a}[\text{Li}_{0.5}\text{Mn}_{1.5}]_{16d}\text{O}_{3.75}$. The final observed, calculated, and difference profiles are shown in Fig. 3a and b, and the refined lattice parameters, atomic coordinates, and thermal parameters are listed in Table 5.

In both models, the Wyckoff site 32e (x, x, x) were occupied by oxygen atoms, while the 8a site (0.125, 0.125, 0.125) were occupied by Li. The 16d site (0.5, 0.5, 0.5) were occupied by Li and Mn. Additionally, 16c site partially occupied by Li were explicitly added in model (1). In both models, the ratio of cations to anions is the same (0.8), and what

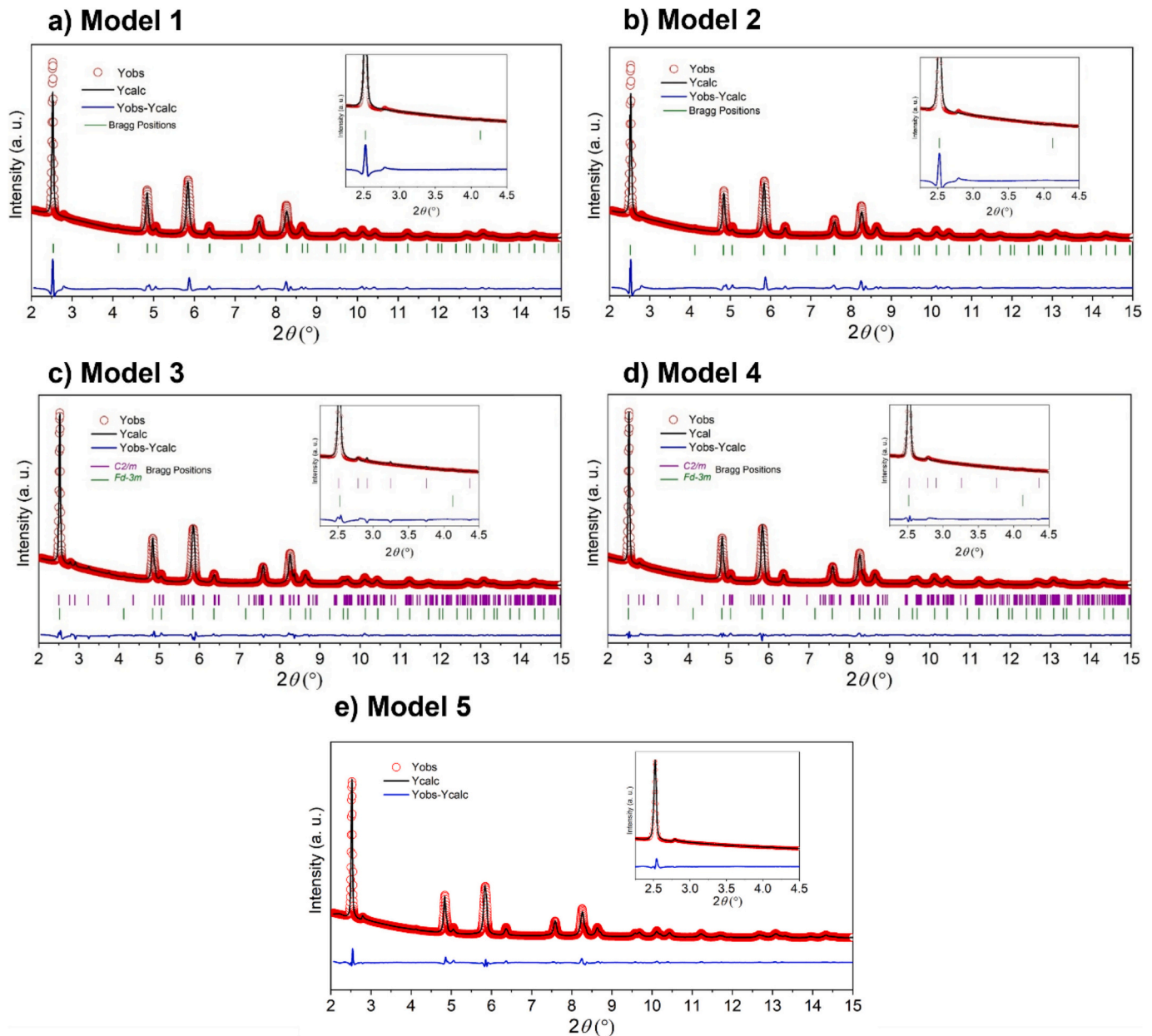


Fig. 3. Rietveld refinements to Synchrotron data, corresponding to models 1 (a), 2 (b), 3 (c), 4 (d), and FAULTS refinement corresponding to model 5 (e).

Table 4

Compositions evaluated in Rietveld Refinements and their atomic distributions.

Model	Phases	Cationic distribution in the cubic-spinel	Nominal composition
1	Cubic (Fd-3m)	(Li) _{8a} [Li _{0.4} Mn _{1.6}] _{16d} [Li _{0.2}] _{16c} O ₄	Li _{1.6} Mn _{1.6} O ₄
2	Cubic (Fd-3m)	(Li) _{8a} [Li _{0.5} Mn _{1.5}] _{16d} O _{3.75}	
3, 4, 5	+ monoclinic (C2/m) Li ₂ MnO ₃	(Li) _{8a} [Li _{0.333} Mn _{1.67}] _{16d} O ₄	Depends on the obtained phase quantification

changes among the models is how the Li ion are distributed within the crystallographic sites, as well as the sites occupancies. The zero shift, scale factors, background points, lattice parameters, U, X, and Y profile shape parameters, oxygen atomic positions, and overall thermal displacements were refined, while occupancies were kept fixed to represent the stoichiometry and atomic distribution among sites (see section 3.4

"Structural Refinements" for more details).

Although the models differ in the relative lithium occupancy of the 16c and 16d sites, the resulting refinements produce virtually indistinguishable intensity fits. This is attributable to lithium's low X-ray scattering factor, which renders changes in Li occupancy only a minor contribution to the overall diffracted intensity. Importantly, both refinements fail to reproduce the super-structure reflections associated with the monoclinic Li₂MnO₃ phase, indicating that the Li/Mn ordering responsible for those reflections is not captured by either structural model (Fig. 3a and b, insets).

Model 3 – Introducing a Two-Phase System. From the above results, we postulate that LMO consists not of a single cubic phase with Li in interstices and/or oxygen vacancies as proposed before, but rather in a two phase like system, formed by monoclinic layered Li₂MnO₃ and cubic spinel Li_(1+δ)Mn_(2-δ)O₄. The co-existence of spinel-layered phases at the nano-scale has been reported in the field of Li-rich manganates used as cathodes materials for Li-ion batteries [96–98] and supports this hypothesis.

Table 5

Reliability factors, unit cell parameters, atomic positions and occupations used in Rietveld refinements of LMO using single phase models based on cubic spinel, space group $Fd-3m$ (models 1 and 2). The obtained parameters with estimated standard deviations given in brackets were refined.

(Li) _{8a} [Li _{0.4} Mn _{1.6}] _{16d} [Li _{0.2}] _{16c} O ₄ ($R_{wp} = 18.5$, $R_{Bragg} = 2.88$)							
$a = 8.132(2) \text{ \AA}$; $B_{ov} = -0.6(1) \text{ \AA}^2$							
Atom	Type	Site	x	y	z	O _{cc} ^a	B _{iso}
Li [1]	Li	8a	0.125	0.125	0.125	0.04167	1.18
Li [2]	Li	16d	0.5	0.5	0.5	0.01374	0.78
Li [3]	Li	16c	0	0	0	0.01388	0.78
Mn	M ⁴⁺	16d	0.5	0.5	0.5	0.06958	0.78
O [1]	O ²⁻	32e	0.261(1)	0.261(1)	0.261(1)	0.16667	1.51
(Li) _{8a} [Li _{0.5} Mn _{1.5}] _{16d} O _{3.75} ($R_{wp} = 18.8$, $R_{Bragg} = 3.01$)							
$a = 8.131(1) \text{ \AA}$, $B_{ov} = -0.6(1) \text{ \AA}^2$							
Atom	Type	Site	x	y	z	O _{cc} ^a	B _{iso}
Li [1]	Li	8a	0.125	0.125	0.125	0.04167	1.18
Li [2]	Li	16d	0.5	0.5	0.5	0.02083	0.78
Mn	M ⁴⁺	16d	0.5	0.5	0.5	0.06250	0.78
O [1]	O ²⁻	32e	0.261(1)	0.261(1)	0.261(1)	0.15625	1.51

^a Occupation numbers are relative to the general site with multiplicity 192.

Based on this premise, a new model using a two-phase system was evaluated for the refinement performed to the Synchrotron data, taking into account the (1) mass balance expressed in Eq. 1 and (2) ⁷Li MAS NMR results (discussed above) as additional considerations.

According to the ICP-OES and XAS analysis our material exhibits a bulk Li/Mn ratio of 1.01 ± 0.02 and Mn oxidation state = $4+$ (Table 2). Consequently, for a Li₂MnO₃ secondary phase with a theoretical bulk Li/Mn ratio of 2 and oxidation state of Mn = $4+$, the spinel fraction must have a bulk Li/Mn ratio < 1 and the Mn must have oxidation state $4+$. Having this in mind, and the ⁷Li MAS NMR results that suggested the presence of the spinel with composition Li_{1.33}Mn_{1.67}O₄, this cubic phase (ICDD 1514017, space group = $Fd-3m$, N° 227) was used for the Rietveld refinements and phase quantification performed to the Synchrotron data. The Wyckoff site 32e of the spinel was fully occupied by oxygen atoms and the 8a site (0.125, 0.125, 0.125) by Li. 16d site (0.5, 0.5, 0.5) were occupied by Mn (83.5%) and Li (16.5%). Site exchange was allowed, keeping constant the total amount of Li and Mn. The refined values, considering the standard deviations, did not differ from the starting values, pointing to a realization of the Li_{1.33}Mn_{1.66}O₄ composition for the cubic spinel phase.

A secondary phase with monoclinic structure and stoichiometry Li₂MnO₃ (special group = $C2/m$, N° 12, ICDD 1514044) was added.

The final observed, calculated, and difference profiles are shown in Figs. 3c, while the refined lattice parameters, atomic coordinates, and thermal parameters are listed in Table 6.

On the one hand, there was an improvement in terms of the interpretation of this pattern using the dual-phase system, since the superstructure reflections are now modeled. Furthermore, as it is shown in Table 6, the refined lattice parameters for the cubic spinel and monoclinic phases are comparable to those reported in bibliography. For example, the cubic spinel, the value of $8.142 \text{ \AA}$ is identical to that obtained for well crystallized Li_{1.33}Mn_{1.67}O₄ spinel [3,4,99] underpinning our hypothesis that this could be the actual composition of the cubic phase in our system. Rietveld refinement of the combined spinel + layered model yielded weight fractions of 84(5) % spinel and 16(3) % layered (Table 6). However, as shown in the inset of Fig. 3c, the region between 2.6° and 4° 2θ , containing the reflections commonly attributed to the Li₂MnO₃ superstructure, remains poorly fitted. In particular, the reflections indexed as 020, 110, -111 , 021 and 111, in the $C2/m$ structure (Fig. 1b) exhibit substantial broadening due to extensive stacking-fault disorder, a characteristic feature of layered Li₂MnO₃ that cannot be adequately described by conventional Rietveld refinement. Except for the stacking-fault-broadening, no size-broadening effects (e. g. nanoscale phases) were observed, in agreement with the NMR results

Table 6

Reliability factors, unit cell parameters, atomic positions and occupations used in the Rietveld refinement of the cubic-Li_{1.33}Mn_{1.67}O₄ and monoclinic-Li₂MnO₃ system ($R_{wp} = 11.2$) (model 3).

Cubic Li _{1.33} Mn _{1.67} O ₄ ($Fd-3m$) spinel phase ($R_{Bragg} = 3.75$)							
$a = 8.142(1) \text{ \AA}$, $B_{ov} = -0.6(1) \text{ \AA}^2$							
Mass fraction = 84(5) %							
Atom	Type	Site	x	y	z	O _{cc} ^a	B _{iso}
Li [1]	Li	8a	0.125	0.125	0.125	0.04167	1.18
Mn	Mn ⁴⁺	8a	0.125	0.125	0.125	-0.00005 (6)	1.18
Li [2]	Li	16d	0.5	0.5	0.5	0.0137(6)	0.78
Mn	Mn ⁴⁺	16d	0.5	0.5	0.5	0.0697(6)	0.78
O [1]	O ²⁻	32e	0.2601 (8)	0.2601 (8)	0.2601 (8)	0.16667	1.51
Monoclinic Li ₂ MnO ₃ ($C2/m$) layered phase							
$a = 4.93(2) \text{ \AA}$; $b = 8.539 (3) \text{ \AA}$; $c = 5.020(2) \text{ \AA}$; $\beta = 109.36(3)^\circ$							
Mass fraction = 16(3) %							
Atom	Type	Site	x	y	z	O _{cc} ^b	B _{iso}
Li [1]	Li	2b	0	0.5	0	0.2135	1.0
Mn	Mn ⁴⁺	2b	0	0.5	0	0.0365	1.0
Li [2]	Li	2c	0	0	0.5	0.25	1.0
Li [3]	Li	4 h	0	0.681	0.5	0.493	1.0
Mn	Mn ⁴⁺	4 h	0	0.681	0.5	0.007	1.0
Li [4]	Li	4 g	0	0.1687	0.0	0.0435	0.5
Mn	Mn ⁴⁺	4 g	0	0.1687	0.0	0.4565	0.5
O [1]	O ²⁻	4i	0.224	0	0.225	0.5	0.5
O [2]	O ²⁻	8j	0.253	0.323	0.2275	1.0	0.5

a. Occupation numbers are relative to the general site with multiplicity 192. b. Occupation numbers are relative to the general site with multiplicity 8.

above and reinforcing the hypothesis of two separate crystalline phases. Therefore, two further approaches, using a two-phases system were evaluated.

Models 4 & 5 – Improving the Fit of the Superstructure Reflections. In order to improve the fit quality, particularly in the region containing the characteristic low-angle reflections of the Li₂MnO₃ phase, two approaches were evaluated using Model 3 as the starting point.

In model 4, special reflections associated with the layered Li₂MnO₃ phase were explicitly added. Full Prof offers the possibility to introduce special reflection half-width parameters for individual reflections [100]. The Gaussian full-width at half maximum (FWHM) is then modified according to $FWHM^2 = FWHM^2(RP) + D_{HG}^2$, the Lorentzian FWHM according to $FWHM = FWHM(RP) + D_{HL}$, and the position according to $2\theta = 2\theta(RP) + D_{pos}$.

In this approach, special reflection half-width parameters have been introduced and refined for the 111 reflection of the Li_{1.33}Mn_{1.67}O₄ spinel main phase with $Fd-3m$ space group: $D_{HG}^2 = 0.0007(1)$, $D_{HL} = -0.12(1)$, $D_{pos} = -0.006(1)$. Furthermore, since the superstructure reflections belonging to Li₂MnO₃ phase (here located in the 2θ range from about 2.5 to 4.5°) do not exhibit the same FWHM parameters as all the other main reflections from Li₂MnO₃, additional Gaussian FWHM parameters have been refined for the 020 reflection ($D_{HG}^2 = 0.010(13)$) and with a single constrained value for the reflections 110, -111 , and 021 ($D_{HG}^2 = 0.03 (2)$). Fig. 3d presents the final, observed, calculated, and difference profiles while the refined lattice parameters, atomic coordinates, and thermal parameters are listed in Table 7. It can be seen that this new approach improved the visual fit, that was expressed also in better reliable factors (R_{wp} and R_{Bragg}), and smaller standard deviations.

Finally, in model 5, Li₂MnO₃ was treated using the FAULTS program [15,101,102]. FAULTS models the structure of a layered phase as a stack of atomic layers linked by stacking vectors with a certain probability, allowing explicit refinement of the stacking-fault probabilities. In this model, the scale factor of the spinel-cubic contribution obtained in

Table 7

Reliability factors, unit cell parameters, atomic positions and occupations used in the Rietveld refinement of the cubic-Li_{1.33}Mn_{1.67}O₄ and monoclinic-Li₂MnO₃ system ($R_{wp} = 7.25$) using special reflections (model 4).

Cubic Li _{1.33} Mn _{1.67} O ₄ (<i>Fd-3m</i>) spinel phase ($R_{Bragg} = 1.93$)							
$a = 8.1501(8) \text{ \AA}$, $B_{ov} = -0.66(5) \text{ \AA}^2$							
Mass fraction = 85(2) %							
Atom	Type	Site	x	y	z	O _{cc} ^a	B _{iso}
Li [1]	Li	8a	0.125	0.125	0.125	0.04167	1.18
Mn [1]	Mn ⁴⁺	8a	0.125	0.125	0.125	-0.0002 (2)	1.18
Li [2]	Li	16d	0.5	0.5	0.5	0.0137(2)	0.78
Mn [2]	Mn ⁴⁺	16d	0.5	0.5	0.5	0.0694(2)	0.78
O [1]	O ²⁻	32e	0.2613 (4)	0.2613 (4)	0.2613 (4)	0.16667	1.51
Monoclinic Li ₂ MnO ₃ (<i>C2/m</i>) layered phase							
$a = 4.934(1) \text{ \AA}$; $b = 8.542(2) \text{ \AA}$; $c = 4.985(1) \text{ \AA}$; $\beta = 108.93(2)^\circ$							
Mass fraction = 15(2) %							
Atom	Type	Site	x	y	z	O _{cc} ^b	B _{iso}
Li [1]	Li	2b	0	0.5	0	0.2135	1.0
Mn [1]	Mn ⁴⁺	2b	0	0.5	0	0.0365	1.0
Li [2]	Li	2c	0	0	0.5	0.25	1.0
Li [3]	Li	4 h	0	0.681	0.5	0.493	1.0
Mn [2]	Mn ⁴⁺	4 h	0	0.681	0.5	0.007	1.0
Li [4]	Li	4 g	0	0.1687	0.0	0.0435	0.5
Mn [3]	Mn ⁴⁺	4 g	0	0.1687	0.0	0.4565	0.5
O [1]	O ²⁻	4i	0.224	0	0.225	0.5	0.5
O [2]	O ²⁻	8j	0.253	0.323	0.2275	1.0	0.5

a. Occupation numbers are relative to the general site with multiplicity 192. b. Occupation numbers are relative to the general site with multiplicity 8.

model 3 was refined, as well as the scale factor, unit-cell dimensions, profile parameters and stacking vectors probabilities (α) of the layered phase. A description of initial atomic positions, layers and stacking vectors used to describe this phase is shown in Appendix B, Table B1. At an initial state, simulated diffractograms were calculated. In Appendix B, Fig. B2 the effect of increasing stacking-faults probabilities in the broadening of superstructure reflections can be seen. The final observed, calculated, and difference profiles are shown in Fig. 3e, while the refined parameters are presented in Table 8.

After the refinement, an approximated [101] mass fraction of 80.5% and 19.5% for the spinel and layered phases was obtained, respectively. The stacking fault probability obtained after the refinement ($\sim 50\%$) was consistent with previously reported models for Li₂MnO₃ [102]. The refinement successfully reproduced the $2.6^\circ < 2\theta < 4^\circ$ region (Fig. 3e, inset), containing the Li₂MnO₃ superstructure reflections phase.

The usage of FAULTS program allowed us to confirm the presence of Li₂MnO₃ phase with high degree of defects, explaining its weak developed reflections in XRD and the reason why its identification in experimental patterns is not straightforward.

Summarizing, from Rietveld and FAULTS refinement of structure models, based on diffraction data, we postulate that what is labelled as Li_{1.6}Mn_{1.6}O₄ throughout the literature is not a single, pure spinel phase but a two-phases system consisting of a Li-deficient cubic spinel (≈ 80 wt

%) and a monoclinic, Li-rich Li₂MnO₃ phase (≈ 20 wt%) containing significant stacking-fault disorder. While the lithium rich cubic spinels with general formula Li_(1+ δ)Mn_(2- δ)O₄ like Li_{1.33}Mn_{1.67}O₄ present lithium ions at tetrahedral 8a and part of the octahedral 16d site, with manganese ions residing in the octahedral 16d site, the crystal structure of monoclinic Li₂MnO₃ consists of alternating (Li)₂ and (LiMn)₂ layers in which the MO₆ octahedra share common edges. Both phases have structurally similar oxygen sub-lattice making its structural integration feasible at an atomic to a nano-meter length scale lattices [98]. The coexistence of these phases explains the apparent lithium excess in the overall formula and resolves the long-standing discrepancy in the literature, where no crystallographic information file exists for a genuine Li_{1.6}Mn_{1.6}O₄ spinel. To further solidify our conclusions, DFT calculations were performed to investigate thermodynamically favored phases for various Li_xMn_yO₄ compositions.

4.2. DFT

4.2.1. Thermochemical stability analysis

In order to shed light on the possible structural nature of a material with nominal composition Li_{1.6}Mn_{1.6}O₄, the theoretical stability of different crystallo-chemical possibilities was addressed.

As discussed above, interpreting Li_{1.6}Mn_{1.6}O₄ as pure Li-rich spinel would involve placing Li at the 16c site in addition to Li substitution at the 16d site. Another option that preserves the vacant 16c site is Li_{1.6}Mn_{1.6}O₄ = (16/15) Li_{1.5}Mn_{1.5}O_{3.75}, although this option introduces oxygen vacancies. Both structures are worth analyzing in terms of their structural stability and thermodynamic tending.

The stability of all compositions studied in this work were compared by the differences of formation energies of each spinel versus a linear combination of the different possible products of reaction (R1-R6). Those products have been chosen according to the experimental results and the bibliography, taking into account that both Li₂O and MnO₂ could be in small amounts being neglected in XRD. Considering the R1-R6 it is then possible to build equation systems to find a-d parameters which satisfy the equalities.

Li/Mn ratio		
0.5	LiMn ₂ O ₄ $\rightarrow$ aLi ₂ MnO ₃ + bMnO ₂ + cLi ₂ O	(R1)
0.75	Li _{1.25} Mn _{1.75} O ₄ $\rightarrow$ aLiMn ₂ O ₄ + bLi ₂ MnO ₃ + cMnO ₂ + dLi ₂ O	(R2)
0.93	Li _{1.625} Mn _{1.75} O ₄ $\rightarrow$ aLiMn ₂ O ₄ + bLi ₂ MnO ₃ + cMnO ₂ + dLi ₂ O	(R3)
1	Li _{1.625} Mn _{1.625} O ₄ $\rightarrow$ aLiMn ₂ O ₄ + bLi ₂ MnO ₃ + cMnO ₂ + dLi ₂ O	(R4)
1	Li _{1.5} Mn _{1.5} O _{3.75} $\rightarrow$ aLiMn ₂ O ₄ + bLi ₂ MnO ₃ + cMnO ₂ + dLi ₂ O	(R5)
1.08	Li _{1.75} Mn _{1.625} O ₄ $\rightarrow$ aLiMn ₂ O ₄ + bLi ₂ MnO ₃ + cMnO ₂ + dLi ₂ O	(R6)

Fig. 4 shows the formation energy for a given spinel as a function of the composition for reactions R1-R6. All of the energies are relative to the spinel with lower E_F, which was assessed to 0 eV. The Fig. 4 also shows if some linear combinations thermodynamically more stable exist for each composition, and it is used as an indicator for stability or decomposition. Then, $\Delta E_F = E_{F\text{-Spinel}} - E_{F\text{-LC}}$, with E_{F-Spinel} as the E_F for the given spinel and E_{F-LC} as the E_F for the linear combination that satisfied that composition. Thus, the stability criteria is ΔE_F rather than E_F; if $\Delta E_F > 0$, the spinel is unstable, tending to decompose to the linear combination of possible structures with the same overall composition and lower formation energy.

In Fig. 4, the structures written in green are stable, the red ones are unstable, while the blue ones correspond to the decomposition products. The green dotted line represents the convex hull, indicating that by extrapolating all the stoichiometry spinels for $\delta \leq 0.33$ would be stable.

At Li/Mn ratio = 1, the spinel with Li in 16c representation Li_{1.625}Mn_{1.625}O₄ is the global minima in the hull convex, which indicates that is the most stable phase without tending to decomposition. However, around Li/Mn ratio = 1 the E_F practically does not change significantly but the structures tend to decompose. At Li/Mn ratio = 0.93, the Li_{1.625}Mn_{1.75}O₄ composition is unstable, tending to decompose to

Table 8

Initial and final values of refined cell parameters and stacking probabilities (α) ($R_F = 2.53$) obtained using FAULTS program (model 5).

Refined parameters	Initial values	Final values (standard deviation)
a	4.92	4.946(1)
b	8.53	8.536(4)
c	4.75	4.705(3)
$\alpha_{11}, \alpha_{22}, \alpha_{33}$	1	0.50(1)
$\alpha_{12}, \alpha_{13}, \alpha_{21}, \alpha_{23}, \alpha_{31}, \alpha_{32}$	0	0.249(5)

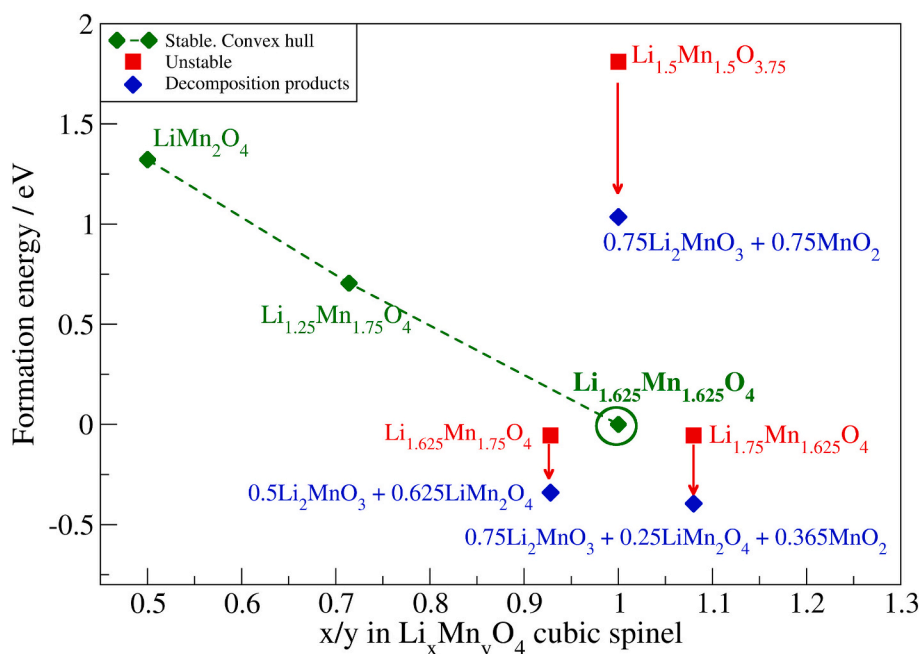


Fig. 4. Formation energies for cubic spinel lithium-manganate oxides as a function of Li/Mn ratio.

$\text{Li}_2\text{MnO}_3 + \text{LiMn}_2\text{O}_4$ mixture by 0.32 eV. The same occurs at $\text{Li}/\text{Mn} = 1.08$, in which $\text{Li}_{1.75}\text{Mn}_{1.625}\text{O}_4$ decomposes to $\text{Li}_2\text{MnO}_3 + \text{LiMn}_2\text{O}_4 + \text{MnO}_2$ by 0.21 eV. This indicates that the stability at $\text{Li}/\text{Mn} = 1$ is highly sensitive to the Li/Mn ratio, with metastable spinels close to the convex hull for that composition range.

The spinel $\text{Li}_{1.5}\text{Mn}_{1.5}\text{O}_{3.75}$ has the highest formation energy but also is highly unstable, tending to decompose to $\text{Li}_2\text{MnO}_3 + \text{MnO}_2$ mixture, which is favored by 0.805 eV. Experimentally, the strategies to obtain spinels with oxygen vacancies, involves high temperature and Ar synthesis and often quenching to cryogenic liquids, which is not the case for the present work.

In addition to Li_2MnO_3 structure, LiMn_2O_4 is expected as a decomposition product for the unstable phases, in agreement with the NMR characterization. According to the decomposition products, although the presence of MnO_2 as a product would be also expected, but its absence in XRD may be given by its low crystallinity, nanodomains regions, presence of different allotropes, and/or amorphous phases, among others.

In summary DFT-based thermochemical analysis indicates that the spinel phases with Li/Mn ratio = 0.5, 0.7 and 1 are stable, with $\text{Li}_{1.625}\text{Mn}_{1.625}\text{O}_4$ as the minimum of the hull convex. However, the presence of Li_2MnO_3 and LiMn_2O_4 as secondary phases evidenced experimentally in this work and the predicted unstable spinel phases for Li/Mn ratio = 0.93 and 1.08, reveal that the stability could be affected by slight imbalances in the Li content, Li/Mn heterogeneities in the sample, among others. The fact that Li_2MnO_3 is experimentally observed as a secondary phase indicates that its formation is not kinetically inhibited under the employed synthesis conditions.

4.2.2. Electronic structure

The projected density of states (pDOS) plot of Mn and O atoms for different structures is shown in Fig. 5. Although the projection is performed using spherical harmonics, which introduces a partial mixing between t_{2g} and e_g manifolds, the main features can still be interpreted in terms of crystal-field splitting. When referred to the stoichiometric LiMn_2O_4 (Fig. 5a), the pDOS can be qualitatively separated into lower-energy and higher-energy energy regions as t_{2g} and e_g -like states by comparison of their relative energetic positions.

LiMn_2O_4 exhibits occupied 3d t_{2g} -like states below the Fermi level

and e_g -like states in its vicinity, as expected for a mixed $\text{Mn}^{3+}/\text{Mn}^{4+}$. This suggests a $\text{Mn}^{4+} - t_{2g}^3 e_g^0$ -like and $\text{Mn}^{3+} - t_{2g}^3 e_g^1$ -like electronic configuration [103,104].

On the other hand, the pDOS of $\text{Li}_{1.25}\text{Mn}_{1.75}\text{O}_4$ (Fig. 5b), $\text{Li}_{1.625}\text{Mn}_{1.625}\text{O}_4$ (Fig. 5c), $\text{Li}_{1.625}\text{Mn}_{1.75}\text{O}_4$ (Fig. 5d) and $\text{Li}_{1.75}\text{Mn}_{1.625}\text{O}_4$ (Fig. 5e) display a clear separation of the occupied- t_{2g} and unoccupied e_g states (i.e. a splitting of the 3d- t_{2g} and e_g states below and above the Fermi level) that is consistent with a more $\text{Mn}^{4+} - t_{2g}^3 e_g^0$ -like electronic configuration. Although in $\text{Li}_{1.625}\text{Mn}_{1.675}\text{O}_4$ and $\text{Li}_{1.75}\text{Mn}_{1.625}\text{O}_4$ a slightly boarder distribution of the electronic states near the Fermi level become more disordered, and more pronounced Mn-3d/O-2p hybridization, the overall electronic structure remains qualitatively similar to $\text{Li}_{1.25}\text{Mn}_{1.75}\text{O}_4$.

In contrasts, the introduction of oxygen vacancies in $\text{Li}_{1.5}\text{Mn}_{1.5}\text{O}_{3.75}$ (Fig. 5f) leads to significant modifications in the electronic structure, particularly near the Fermi level. New states emerge with mixed Mn-3d and O-2p character, indicating enhanced covalency and the formation of defect-induced electronic states. This behavior suggests that charge compensation is not solely accommodated by changes in the Mn oxidation state, but also involves oxygen states, pointing toward partial anionic redox activity. This electronic feature suggests an intrinsic tendency toward oxidative decomposition.

The pDOS of Li_2MnO_3 (Fig. C4) is consistent with the formal Mn^{4+} (d^3) configuration, with the Mn-3d states predominantly occupying the t_{2g} manifold while the e_g states remain essentially unoccupied. The absence of significant Mn^{3+} -like e_g occupation is consistent with the high oxidation state and stable electronic configuration of Mn in this phase.

Correlating the electronic density of states with the convex-hull diagram reveals a clear relationship between the position of the Mn-derived states and the thermodynamic stability of the structures. In particular, the presence of Mn states close to the Fermi level is associated with energetically unfavorable Li-rich phases. The stable phases exhibit a band gap of approximately 0.7 eV between the occupied and unoccupied Mn-derived states, whereas the unstable phases display significantly smaller gaps, below 0.35 eV. This reduced separation between occupied and unoccupied Mn states indicates a greater tendency toward Mn oxidation, favoring the stabilization of Mn^{4+} species, as observed for Li_2MnO_3 and MnO_2 , as proposed in Fig. 4 and based on the experimental

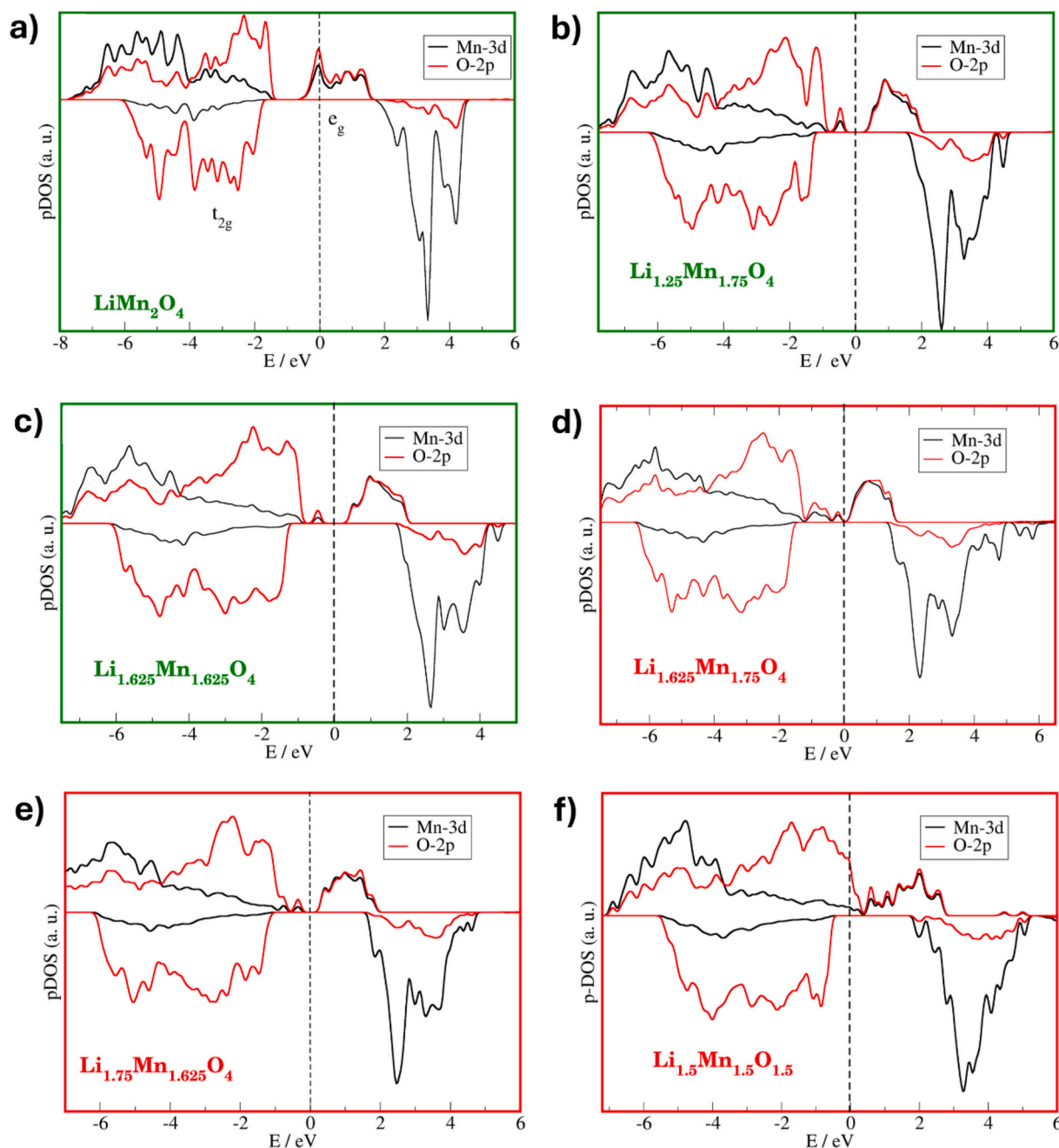


Fig. 5. Projected density of states (pDOS) of the 3d-Mn/2p-O states for the different cubic spinel-based structures. The energy scale is referenced to the Fermi level (FL = 0 eV), marked by the dashed vertical lines.

evidence.

In terms of the sorbent properties the coexistence of Li_2MnO_3 and $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ implies that the experimentally prepared sorbent is structurally heterogeneous, which may influence the subsequent Li^+/H^+ exchange and Li uptake. It is well known that under acid condition Li_2MnO_3 tends to transform to alpha and gamma MnO_2 , resulting in an irreversible loss in lithium uptake capacity [105].

4.2.3. Mn—O₆ distortions

In order to capture the polyhedral MnO_6 geometry changes for the structures with different Li content, the pair radial distribution function $g(r)$ of Mn—O₆ polyhedral for distances lower than 3 Å are analyzed (Fig. 6).

Stoichiometric LiMn_2O_4 exhibits two main Mn—O distance populations centered at 1.95 and 2.05 Å. These distances are distributed

over the axial and equatorial axes. The set of distances of 2.05 Å indicates an elongated Mn—O bond, compatible with the Jahn-Teller (JT) effect. LiMn_2O_4 nominally contains equal amounts of Mn^{3+} and Mn^{4+} , the first Mn—O coordination shell remains relatively narrow, suggesting that JT distortions are dynamically averaged within the cubic spinel structure.

Compared with stoichiometric LiMn_2O_4 , both $\text{Li}_{1.25}\text{Mn}_{1.75}\text{O}_4$ and $\text{Li}_{1.625}\text{Mn}_{1.625}\text{O}_4$ exhibit an increased population Mn—O bonds at $r \sim 1.95$ Å, indicating a lower composition of enlarged Mn—O bonds and mitigation of JT effect. However, a small population of Mn—O short distances (~ 1.8 Å) and long distances (~ 2.18 Å) peaks out, indicating a distortion of a few octahedral. These distortions belong to ${}_5\text{O}[\text{Mn}]\text{—O}[\text{Li}]\text{O}_5$ substructures. It is important to denote the longest Mn—O distances population for $\text{Li}_{1.625}\text{Mn}_{1.75}\text{O}_4$ and $\text{Li}_{1.75}\text{Mn}_{1.625}\text{O}_4$ ($r > 2.2$ Å). Together with the increased occupation of the e_g -like states observed in

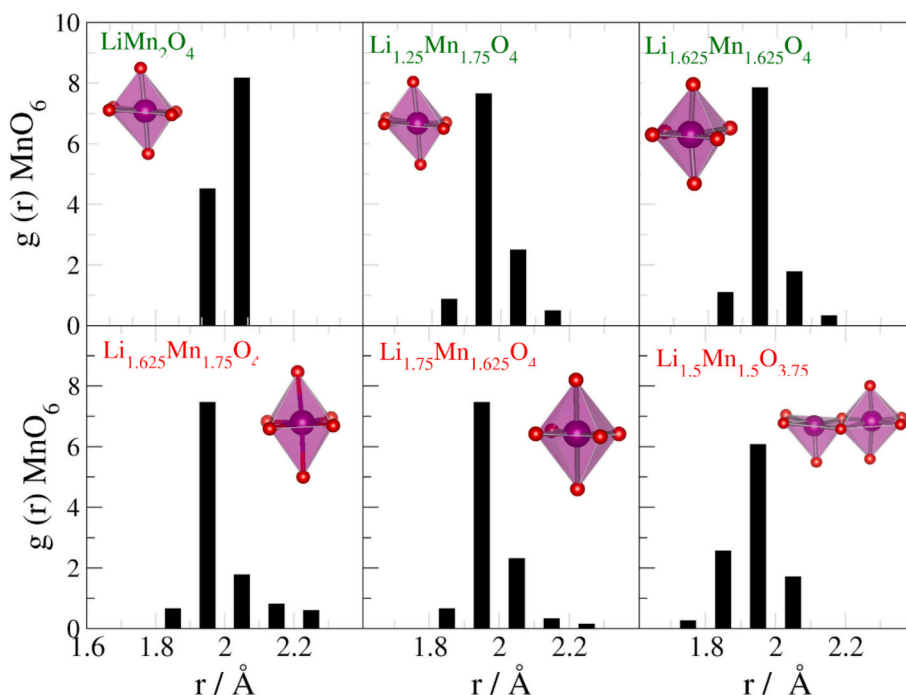


Fig. 6. Pair radial distribution $g(r)$ of Mn—O as a function of distance r for different spinels.

the pDOS, these distortions might affect drastically the stability, triggering decomposition reactions.

$\text{Li}_{1.5}\text{Mn}_{1.5}\text{O}_{3.75}$ displays a markedly different behavior, characterized by multiple Mn—O coordination shells below 2.05 Å, including very short Mn—O distances ($r < 1.8$ Å). This suggests that oxygen vacancies induce local coordination, with more complex structural rearrangement beyond conventional JT distortions.

5. Conclusion

This study provides a comprehensive structural reassessment of lithium manganese oxide with a nominal composition of $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$, a material long assumed to form a pure, single-phase cubic spinel. Our combined analytical approach demonstrates that synthesis pathways involving Li/Mn ratios near unity produce a coexisting phase mixture rather than a monolithic structure. Specifically, we found a Li_2MnO_3 secondary phase (ca. 20%) alongside $\text{Li}_4\text{Mn}_5\text{O}_{12}$ ($\text{Li}_{1.33}\text{Mn}_{1.66}\text{O}_4$), a combination that collectively preserves both the nominal bulk stoichiometry and the target Mn^{4+} oxidation state. This finding relies on the synergistic pairing of ^7Li MAS NMR spectroscopy to probe local lithium environments with high-resolution synchrotron X-ray diffraction to quantify phase fractions, that support a two-phase structural model. The model can be further refined by taking stacking faults into account.

Complementary density functional theory (DFT) calculations confirm that while a pure nominal cubic spinel with lithium in the 16c site is thermodynamically possible, its proximity to unstable phases makes it highly sensitive to minor synthetic and stoichiometric variations. Consequently, phase separation and the formation of secondary Li_2MnO_3 are highly favourable under experimental conditions with Li/Mn ratios near unity. Furthermore, it appears that the dissolution of this secondary phase during the acid activation of LMO to HMO has been overlooked so far as a potential factor influencing extraction performance. A 20% loss of the initial ion-exchange matrix through sacrificial dissolution leaves the remaining spinel phase with altered porosity and higher surface area. These insights provide a critical foundation for revisiting synthetic strategies, optimizing structural stability, and accurately evaluating the long-term cycling performance of lithium-excess manganese oxides tailored for direct lithium extraction (DLE)

applications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2026.140357>.

Data availability

Link to Zenodo Provided

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