The Li$_3$Ru$_y$Nb$_{1-y}$O$_4$ (0 ≤ y ≤ 1) System: Structural Diversity and Li Insertion and Extraction Capabilities

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**ABSTRACT:** Searching for novel high-capacity electrode materials combining cationic and anionic redox processes is an ever-growing activity within the field of Li-ion batteries. In this respect, we report on the exploration of the Li$_3$Ru$_y$Nb$_{1-y}$O$_4$ (0 ≤ y ≤ 1) system with an O/M ratio of 4 to maximize the number of oxygen lone pairs, responsible for the anionic redox. We show that this system presents a very rich crystal chemistry with the existence of four structural types, which derive from the rocksalt structure but differ in their cationic arrangement, creating either zigzag, helical, jagged chains or clusters. From an electrochemical standpoint, these compounds are active on reduction via a classical cationic insertion process. The oxidation process is more complex, because of the instability of the delithiated phase. Our results promote the use of the rich Li$_3$MO$_4$ family as a viable platform for a better understanding of the relationships between structure and anionic redox activity.

### INTRODUCTION

Energy storage is of crucial importance to boost the use of renewable energies and facilitate the deployment of electric transportation, both of which will contribute to a reduction in CO$_2$ emission. Rechargeable batteries can power electric vehicles and can be recharged by electrical energy generated by wind, solar, or nuclear energy, thus eliminating the use of petroleum. An important step in the evolution of the energy storage using rechargeable batteries was the development of the Li-ion batteries, whose concept and commercialization date back to 1980 and 1991, respectively. The Li-ion battery technology is considered to be the most promising of all existing technologies, because of its high volumetric and gravimetric energy density, which can reach 600 Wh/L. However, users constantly call for better performance to achieve, for instance, longer driving distances. To enhance the energy density of Li-ion batteries, huge research efforts are currently devoted to lanarrric electrodes and, more specifically, to the layered Li$_3$Mn$_{0.53}$Co$_{0.13}$Ni$_{0.13}$O$_2$ phases, which are termed Li-rich NMC and show capacities exceeding 280 mAh/g, compared to 180 mAh/g for the LiNi$_{0.5}$Mn$_{0.2}$Co$_{0.3}$O$_2$ (NMC) phases used in today’s commercial batteries. However, their practical use is plagued by capacity and voltage decays.

The extra capacity pertaining to the Li-rich NMC was shown, via the study of model systems by our group in 2013, to be nested in the participation of the anionic network (2O$^{2-}$ ↔ O$_2^{2-}$) to the overall redox reaction process. This finding has received worldwide attention, both experimentally and theoretically. Studies on disordered rocksalt structures, such as Li$_3$Mn$_{0.5}$Nb$_{0.3}$O$_2$ or Li$_3$Mn$_{0.4}$Nb$_{0.3}$O$_2$ and, more recently, on the three-dimensional β-Li$_3$IrO$_4$ have shown that anionic redox activity can occur in many rocksalt-based oxides, independently of their structural dimensionality. Various theoretical calculations were also performed to rationalize the science at work in these new electrode materials. They all stressed the key role played by the localized nonbonding oxygen 2p levels (e.g., oxygen lone pairs) with, namely, their relative positions with respect to the cationic d-levels. By pushing these calculations further, Xie et al. have lately shown that the amount of oxygen lone pairs can be tuned by manipulating the atomic oxygen/metal ratio composition at high O/M ratio, less oxygen is bonded to metal and, therefore, there are more nonbonding oxygen states in the material. Altogether, these studies have led to a sound scientific platform for designing high-capacity oxide electrodes by acting either on the structural...
dimensionality or on the material’s composition via tuning of the O/M ratio.

Along this line, Yabuuchi et al. studied the electrochemical properties of rocksalt-based Li3NbO4 compounds against oxidation, but did not observe any activity, most likely due to the insulating character of the Li3NbO4. To successfully alleviate this issue, the authors partially substituted Nb by 3d metals with the best results obtained for Mn,

rather that an insulating Li3NbO4 phase and studying the insulating character of the Li3NbO4. To successfully alleviate this issue, the authors partially substituted Nb by 3d metals with the best results obtained for Mn, but surprisingly the authors did not report the electrochemical properties of their compounds under reduction. To widen the spectrum of oxides while pursuing the same objective, we herein report a their compounds under reduction. To widen the spectrum of oxides while pursuing the same objective, we herein report a

through this study, we unveiled the rich crystal chemistry of the Li3RuNb1−xO4 (0 ≤ y ≤ 1) series, which counts four rocksalt-type structures made of LiO6 and MO6 (M = Ru or Nb) octahedra sharing edges with different cation distributions. From an electrochemical standpoint, these compounds can be either oxidized or reduced with an activity (200 mA/h/g) on reduction associated with the cationic Ru5+/Ru4+ and Ru4+/Ru3+ redox couples and a large activity on oxidation (300 mA/h/g), for which the charge compensation is still unclear, but likely involves oxygen redox. For reasons of clarity, the paper will be structured as follows. We first report the synthesis and structural determination of the pristine phases as a function of their Nb content, and then we present their electrochemical properties upon reduction, together with the structure of the new reduced phases. Finally, we show the oxidative behavior of these phases prior to entering into a rationalization of the structural and electrochemical properties in the Discussion section.

■ EXPERIMENTAL SECTION

Synthesis. Classical solid-state synthesis from the oxide precursors, Nb2O5 (Sigma−Aldrich, 99.9%) and RuO2 (Alfa Aesar, 99.9%) and with 10% excess Li2CO3 (Sigma−Aldrich, 99%), was employed to prepare the Li3Ru0.5Nb0.5O4 compounds with y = 1, 0.7, 0.5, 0.3, 0.1, 0. These compositions were chosen to obtain a representative view of the phase diagram. The reactants were mixed using mortar and pestle before grinding in a planetary ball mill, using a zirconia set for 1 h at 600 rpm. After pelletizing the react mix, the pellets were fired for 24 h at 900 °C in air. The samples then were ground again, pelletized, and fired at 900–1000 °C, with the exception of ruthenium-rich compounds (y = 1 and y = 0.7), because they suffer from reduction upon prolonged heating. This step was repeated until pure phases were obtained. Heat treatment conditions for each sample are reported in Table S1 in the Supporting Information. Scanning electron microscopy/energy-dispersive X-ray (SEM/EDX) analysis was carried out on the prepared powders to probe the Ru/Nb ratio and confirmed the expected stoichiometries (see Table S1).

Crystal Structure Analysis. Synchrotron X-ray diffraction measurements (SRXD) were performed on the 11-BM beamline of the Advanced Photon Source at Argonne National Laboratory, with a wavelength of 0.439239 Å for Li3RuO4 and 0.414617 Å for the other samples. The powder was mixed with an appropriate amount of amorphous silica to limit absorption, and placed in a Kapton capillary (diameter of 0.7 mm). Ex situ samples, air-sensitive, were sealed in a Kapton capillary samples. The powder was mixed with an appropriate amount of amorphous silica to limit absorption, and placed in a Kapton capillary (diameter of 0.7 mm).

In situ X-ray powder diffraction (XRD) measurements were done using a homemade airtight electrochemical cell equipped with a Be window, using a Bruker D8 Avance diffractometer with Cu Kα radiation (λ(Kα1) = 1.54056 Å, λ(Kα2) = 1.54439 Å) and a Lynxeye detector. Neutron powder diffraction (NPD) patterns were measured on the D1B powder diffractometer at Institut Laue–Langevin (ILL) with λ = 1.2896 Å.

Rietveld refinements were performed using the FullProf program. Both neutron and synchrotron data were refined simultaneously with a similar weight for both patterns. Background was taken into account using Chebyshev polynomials, except for the synchrotron pattern of Li3Ru0.5Nb0.5O4 for which an interpolation of points was used. X-ray and neutron absorption were estimated and taken into account in the refinement.

Samples for transmission electron microscopy (TEM) were prepared by grinding materials in a mortar and dispersing the powder onto holy carbon TEM grids. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images were acquired using a probe aberration-corrected FEI Titan 80-300 microscope operated at 300 kV.

Electrochemical Testing. All the electrochemical characterization was performed in Swagelok-type cells. The positive electrode material was grinded in a SPEX-type ball mill for 15 min with 20% carbon SP before testing. Li metal was used as an anode. Whatmann GF/D borosilicate glass fibers sheets were used as separators, and the electrolyte was LP100-1/1/3 EC/PC/DMC with 1 M LiPF6. Cells were assembled in an argon-filled glovebox. Galvanostatic cycling was performed at C/10 (meaning 1 Li is extracted in 10 h) with different cutoff voltages, depending on the composition of the active material, from 4.2 V to 4.6 V vs Li+/Li. Ex situ samples were washed with DMC inside an Ar-filled glovebox before being dried under vacuum. In situ gas analysis was performed into a special homemade cell, using the same electrode material, electrolyte, and negative electrode as used for the standard electrochemical tests.

■ RESULTS

Structural Determination. While both Li3RuO4 and Li3NbO4 end-members had been reported previously, crystallizing in P 2/a and I 4 3 m space groups, respectively, the Nb for Ru substitution series Li3Ru1−xNb0.5O4 to our knowledge, was never explored. Members of the Li3RuNb1−xO4 series were synthesized via a classical ceramic process. Single-phase compounds with a rich structural diversity, depending on the composition, are obtained. At this point, it is important to recall that Nb and Ru can be hardly distinguished by XRD, as they differ by only three electrons (Z = 41 and 44, respectively). In such cases, neutron diffraction is usually performed; however, neutron scattering lengths of Nb and Ru are very similar (bNb = 7.054 fm and bRu = 7.03 fm), so neutron diffraction cannot give any contrast either. Therefore, we hypothesized a total mixing between Ru and Nb based on their physical similarities.

Figure 1 shows the synchrotron X-ray powder diffraction patterns of several compounds in the yLi3Ru1−yO4 = (1 − y)Li3NbO4 phase diagram. The diffractograms for y = 0.7, 0.5, and 0.3 could be indexed with known structures that differ from those of the end-members. Indeed, Li3Ru0.5Nb0.5O4 and Li3Ru0.7Nb0.3O4 crystallize in the same structure as Ag3RuO4, and Li3Ru0.7Nb0.3O4 is isosstructural to β-Li3TaO4.

Figure 2 summarizes the different structures that we isolated within the Li3Ru1−xNb1−yO4 series. They all derive from the rocksalt structure made of LiO6 and MO6 (M = Ru or Nb, statistically distributed) edge-sharing octahedra. They differ by the distribution of Li and M within the octahedral sites, which changes substantially with niobium concentration, leading to different space groups with different Ru/Nb frameworks. The best way to visualize the Ru/Nb framework transformation is to draw the M−M bonds only (see top of Figure 2). As the niobium content increases, the arrangement of the M−M bonds transforms from [RuO6] zigzag chains in Li3RuO4 to [MO6] spiral chains in Li3Ru0.5Nb0.5O4 for y = 0.7 and y = 0.5.
then to jagged [MO₆] chains in Li₃Ru₀.₃Nb₀.₇O₄, and finally to clusters of four [MO₆] in Li₃Ru₀.₁Nb₀.₉O₄.

To get a better insight into the position of light elements, Li and O, we performed combined Rietveld refinements of synchrotron XRD and neutron powder diffraction data and we used TEM analysis to confirm the proposed structures and characterize the defects at the local scale. First, the two end members will be analyzed and then the focus will be made on the intermediate structures among the yLi₃RuO₄ − (1 − y)Li₃NbO₄ phase diagram. The refinement of Li₃RuO₄ (Figure S1 and Table S2 in the Supporting Information) confirms the structural model proposed by Alexander et al., with the exception that our trials to introduce Li/Ru mixing and/or Li deficiencies as described in ref 22 lead to a worse refinement, compared to a fully ordered model. Complementary transmission electron microscopy data on this sample reveal sparse defects that are related to coherent intergrowths of Li₃RuO₄ structural domains a few tens of nanometers in size, which share the same anionic sublattice but have different crystallographic orientations (see Figure S2 in the Supporting Information). Moreover, no local antisite defects were observed, which is fully consistent with the results of the Rietveld refinement. The SXRD and NPD patterns collected for Li₃NbO₄ were satisfactorily refined (see Figure S3 and Table S3 in the Supporting Information), according to the reported model.¹⁹

Turning to the XRD patterns of the intermediate compounds, one can observe that the patterns of Li₃RuO₄, Li₃Ru₀.₇Nb₀.₃O₄, and Li₃Ru₀.₅Nb₀.₅O₄ initially appear very similar. However, our attempts to fit Li₃Ru₀.₇Nb₀.₃O₄ and Li₃Ru₀.₅Nb₀.₅O₄ using the Li₃RuO₄ model did not lead to a satisfactory result. In contrast, our synchrotron X-ray and neutron diffraction patterns could be perfectly refined with a structural model based on the Ag₃RuO₄ structure,²⁰ in which lithium replaces silver (see Figure 3a). Patterns for both y = 0.7 and y = 0.5 can be fitted in the P 4₁ 2 2 space group, with lattice

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**Figure 1.** Synchrotron X-ray diffraction patterns for the Li₃RuₓNb₁₋ₓO₄ samples with y = 1, 0.7, 0.5, 0.3, 0.1, and 0.

**Figure 2.** Structures of the Li₃RuₓNb₁₋ₓO₄ for y = 1, 0.7, 0.5, 0.3, 0.1, and 0. For each composition, the Ru/Nb frameworks (M–M bonds only) are shown on top of the structures. Space groups and refined cell parameters are indicated at the bottom. In all structures, Ru is gray, Nb is green, Li is yellow, O is red, and Ru/Nb octahedra are gray.
parameters $a = 5.8940(2) \text{ Å}$ and $c = 8.3854(4) \text{ Å}$ (for $y = 0.7$), and $a = 5.9176(7) \text{ Å}$ and $c = 8.3937(4) \text{ Å}$ (for $y = 0.5$). It is worth mentioning that some reflections exhibit peculiar peak shapes in the SXRD patterns that we handled as special reflections in the refinement. They are indicative of a complex microstructure that was further examined using HAADF-STEM.

Table 1. Structural Parameters for $\text{Li}_3\text{Ru}_{0.5}\text{Nb}_{0.5}\text{O}_4$ Deduced from Rietveld Refinement of Combined Synchrotron/Neutron Diffraction Patterns$^a$

<table>
<thead>
<tr>
<th>atom</th>
<th>Wyckoff position</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$B_{iso} (\text{Å}^2)$</th>
<th>occupancy</th>
</tr>
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<tbody>
<tr>
<td>O1</td>
<td>8d</td>
<td>0.2371(5)</td>
<td>0.4905(8)</td>
<td>0.5053(4)</td>
<td>0.92(3)</td>
<td>1</td>
</tr>
<tr>
<td>O2</td>
<td>8d</td>
<td>0.2417(5)</td>
<td>0.9927(7)</td>
<td>1/2</td>
<td>0.53(4)</td>
<td>1</td>
</tr>
<tr>
<td>Ru1/Nb1 (5/5)</td>
<td>4a</td>
<td>0</td>
<td>0.2718(16)</td>
<td>1/2</td>
<td>0.90(4)</td>
<td>0.91(2)</td>
</tr>
<tr>
<td>Li1</td>
<td>4a</td>
<td>0.2592(12)</td>
<td>1/2</td>
<td>3/4</td>
<td>0.90(4)</td>
<td>0.91(2)</td>
</tr>
<tr>
<td>Ru2/Nb2 (5/5)</td>
<td>4b</td>
<td>0</td>
<td>0.747(2)</td>
<td>1/2</td>
<td>0.90(4)</td>
<td>1</td>
</tr>
<tr>
<td>Li3</td>
<td>4b</td>
<td>0.252(2)</td>
<td>1/2</td>
<td>1/4</td>
<td>0.90(4)</td>
<td>1</td>
</tr>
<tr>
<td>Li4</td>
<td>4b</td>
<td>0.5085(2)</td>
<td>1/2</td>
<td>1/4</td>
<td>0.90(4)</td>
<td>1</td>
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$^a$Crystallographic information for $\text{Li}_3\text{Ru}_{0.5}\text{Nb}_{0.5}\text{O}_4$: space group $P 4_1 2 2$; unit-cell parameters of $a = 5.9176(7) \text{ Å}$, $c = 8.3937(8) \text{ Å}$, $Z = 4$, and $V/Z = 73.48 \text{ Å}^3$. Reliability parameters obtained are $R_{\text{Bragg neutrons}} = 5.66\%$, $R_{\text{Bragg SXRD}} = 9.41\%$, $\chi^2_{\text{neutrons}} = 24.46$, and $\chi^2_{\text{SXRD}} = 3.26$.  

![Figure 3](image-url)
images on Li₃Ru₀.₃Nb₀.₇O₄ (see Figures 3c–e). Two main types of defects are observed: (i) (100) antiphase boundaries (APBs), which can be recognized by the shift of the projected spirals along the [010] direction over a/2 (Figure 3d) and (ii) local cooperative variations in the Li/(Ru,Nb) cation ordering pattern (Figure 3e). Turning back to the Rietveld refinement, for both compositions, a partial substitution of Li by the mix Ru/Nb was used to virtually take into account the observed defects. It greatly improves the fit, as can be seen in Figure 3b. Overall, the differences between the two y = 0.7 and y = 0.5 stoichiometries are nested in (i) the cell parameters, which are larger for Li₃Ru₀.₅Nb₀.₅O₄, because of the larger ionic radii of Nb⁵⁺ (0.64 Å), compared to Ru⁵⁺ (0.56 Å), and (ii) greater amount of defects in the y = 0.5 sample, which is detected by the more pronounced Ru/Nb occupancy in the Li₂ site. The final refinements and deduced structural information are shown in Figure 3a and Table 1 for Li₃Ru₀.₅Nb₀.₅O₄ and in the Supporting Information (Figure S4 and Table S4) for Li₃Ru₀.₃Nb₀.₇O₄.

Further increasing the substitution of Ru by Nb leads to the Li₃Ru₀.₃Nb₀.₇O₄ phase, whose diffraction pattern was refined using the structural model of β-Li₃TaO₄ with tantalum being replaced by a statistical mixture of 30% Ru and 70% Nb (see Figures 4a–c). Once again, the defects were identified using TEM. They are related to cooperative variations in the cation ordering (Figure 4d) and were artificially taken into account in the neutron/X-ray refinement by considering a partial substitution between Ru/Nb and Li₂. Table 2 gathers the Li₃Ru₀.₃Nb₀.₇O₄ structural parameters.

Lastly, let us consider the highly substituted Li₃Ru₀.₁Nb₀.₉O₄ phase whose XRD pattern (Figure 1) matches with the one of the Li₃NbO₄ end-member. Indeed, although the pattern contains a tiny contribution of Li₃Ru₀.₃Nb₀.₅O₄ (~3 wt %), it can be fitted with the structural model of Li₃NbO₄ with Nb being partially replaced by 10% Ru. The structure is then described in a cubic unit cell (space group I̅₄ 3 m) with lattice parameter a = 8.44232(1) Å, being twice the one of the basic rocksalt structure. The structure consists of transition-metal clusters composed of four edge-sharing (Ru/Nb)O₆ octahedra. A striking aspect of Li₃Ru₀.₁Nb₀.₉O₄ is the very strong anisotropic peak broadening observed in the SXRD pattern (Figure 5a). It is well-known that the most common sources of

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### Table 2. Structural Parameters for Li₃Ru₀.₃Nb₀.₇O₄ Deduced from Rietveld Refinement of Combined Synchrotron/Neutron Diffraction Patterns

<table>
<thead>
<tr>
<th>atom</th>
<th>Wyckoff position</th>
<th>x</th>
<th>y</th>
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<th>Biso (Å²)</th>
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<td>sf</td>
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<td>sf</td>
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<td>−0.1415(12)</td>
<td>0.8846(12)</td>
<td>1.09(19)</td>
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<tr>
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<td>sf</td>
<td>0.6959(12)</td>
<td>−0.1275(13)</td>
<td>0.3722(11)</td>
<td>0.27(15)</td>
<td>1</td>
</tr>
<tr>
<td>O4</td>
<td>sf</td>
<td>0.9460(10)</td>
<td>−0.1144(11)</td>
<td>0.8895(11)</td>
<td>0.27(15)</td>
<td>1</td>
</tr>
<tr>
<td>Ru1/Nb1  (3/7)</td>
<td>sf</td>
<td>0.0778(3)</td>
<td>−0.1383(2)</td>
<td>0.1247(3)</td>
<td>0.21(2)</td>
<td>0.92(7)</td>
</tr>
<tr>
<td>Li1</td>
<td>sf</td>
<td>0.0778(3)</td>
<td>−0.1383(2)</td>
<td>0.1247(3)</td>
<td>0.21(2)</td>
<td>0.08(7)</td>
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<tr>
<td>Ru2/Nb2  (3/7)</td>
<td>sf</td>
<td>0.5483(18)</td>
<td>−0.1224(19)</td>
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<tr>
<td>Li2</td>
<td>sf</td>
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<td>−0.124(3)</td>
<td>0.631(3)</td>
<td>1.09(4)</td>
<td>1</td>
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Crystallographic information for Li₃Ru₀.₃Nb₀.₇O₄: space group C 2/c; unit-cell parameters of a = 8.425(1) Å, b = 8.428(1) Å, c = 9.343(1) Å, β = 116.503(7)°. Z = 8, and V/Z = 74.22 Å³. Reliability parameters obtained are χ²Bragg neutrons = 4.05%, χ²Bragg SXRD = 7.64%, χ²neutrons = 58.89, and χ²SXRD = 2.92.
Figure 5. (a, b) Rietveld refinement of SRXD pattern of Li$_3$Ru$_{0.1}$Nb$_{0.9}$O$_4$ (a) without considering selective broadening of the reflections and (b) with a selective broadening for peaks that do not comply with \( \frac{h}{2}, \frac{k}{2}, \text{and} \frac{l}{2} \) integer and same parity. Red crosses and black continuous line represent the observed and calculated patterns, respectively. (c–e) HAADF-STEM images of Li$_3$Ru$_{0.1}$Nb$_{0.9}$O$_4$ confirming that the structure is based on tetrahedral units of (Ru,Nb)O$_6$ octahedra and revealing two types of APBs in the material. APB of type 1 and type 2 are marked with white and black arrowheads, respectively. Colored squares highlight translations of the structural domains across the phase boundary, while the black dotted lines show that the (MO$_6$)$_4$ tetrahedra (M = Ru/Nb) tetrahedra are rotated across the boundary. (f) Scheme representing the effect of the antiphase boundaries on the cation ordering for two different rocksalt structures, one with two ordered cations (top) and one with one cation only (bottom), at the atomic scale (left) and at the nanoscopic scale (middle). In (f), the red balls represent oxygen atoms, and the green, yellow and blue balls are cations. The right panel shows the effect of the antiphase domains on the XRD peak shapes.
peak broadening are either the submicrometric size of coherent domains (following the Scherrer equation) or the presence of microstrain (lattice parameter fluctuations from one crystallite to another). In the present case, all our attempts to fit the peak broadening using classical models of anisotropic size and/or strain effects failed. Therefore, a detailed analysis of the relationship between indexation and peak shape was carried out. It appeared that some peaks—namely, those corresponding to NaCl rocksalt subcell $a_{NaCl} = a/2$—are very sharp while the others (superstructure peaks due to ordering between Li and Ru/Nb) are very broad, with a pronounced Lorentzian shape. In the light of this observation, anisotropic broadening of the peaks was taken into account using a selective broadening, depending on $hkl$ indices. All peaks that arise from the rocksalt subcell (whose lattice parameter is $a_{NaCl} = a/2$, where $a$ is the actual lattice parameter of Li$_3$Ru$_0.1$Nb$_0.9$O$_4$), i.e., that comply with the condition “$h/2, k/2, l/2$ integer and same parity”, were kept sharp, and all others were broadened. This resulted in a great improvement of the fit, as can be seen in Figure 5b).

By implementing this broadening depending on $hkl$ indices into the refinement, the average size of coherent domains can be estimated to be $\sim$45 nm. Figure S5 in the Supporting Information shows the final combined refinement against synchrotron and neutron patterns, with the resulting structural parameters reported in Table S5 in the Supporting Information.

TEM analysis of the Li$_3$Ru$_0.1$Nb$_0.9$O$_4$ material confirms the presence of numerous domains with sizes comparable to the average value estimated from SXRD refinement (Figure S6 in the Supporting Information). High-resolution HAADF-STEM data (Figures 5c–e) reveal that these domains are antiphase domains, separated by antiphase boundaries (APB). The positions of the cation columns across an APB are consistent with the basic rocksalt structure, indicating that the APBs leave the anionic sublattice unchanged, but create discontinuity in the pattern of cation ordering. There are two types of APBs in the material, and their atomic arrangement can be derived directly from the [00l] and [011] HAADF-STEM images (see Figures 5c–e). The APBs of type 1 shift one domain, with respect to another, over $a/4$ and introduce a 90° rotation of the structure (see Figure S7 in the Supporting Information). The APBs of type 2 shift the domains over $a/2$ and do not change the orientation of the tetrahedral (MO$_6$)$_4$ units (M = Ru/Nb). Within the domains, the structure preserves perfect cation ordering (Li and Ru/Nb), so that no local antisite defects were observed.

Our XRD and TEM results unambiguously demonstrate that, while the material maintains its rocksalt structure on large coherent domains, the ordering between the cations (Li and Ru/Nb) suffers from the presence of small coherent domains. This is fully consistent with the broadening of the superstructure peaks, while subcell peaks remain sharp, as illustrated in Figure 5f. As a conclusion, the presence of antiphase boundaries and the average size of the antiphase domains can be deduced from the analysis of the XRD pattern. Note that a similar approach has been also recently reported for the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ spinel derivative.24

Overall, the exploration of the Li$_3$Ru$_y$Nb$_{1-y}$O$_4$ has led to a very rich crystal chemistry, enlisting four different single-phase domains having derived rocksalt structures that differ depending on the amount of substituted Nb by (i) the arrangement of the M–M bonds but also by (ii) the nature of the structural defects based on cation ordering, such as the presence of antiphase domains or cooperative variation of cation ordering. Such a structural diversity combined with the progressive emptying of the d-bands and, hence, the disappearance of electronic conduction as we move from Ru$^{5+}$ (3 d electrons) to Nb$^{5+}$ (0 d electron) constitute an attractive playground to further test the robustness of the anionic redox process.

Figure 6. Electrochemical behavior of Li$_3$RuO$_4$, Li$_3$Ru$_0.7$Nb$_0.3$O$_4$, Li$_3$Ru$_0.5$Nb$_0.5$O$_4$, and Li$_3$Ru$_0.3$Nb$_0.7$O$_4$ starting on discharge: (a) voltage versus composition curves for the first cycle at C/10 with cutoff voltages of 1.40, 1.10, 1.05, and 1.00 V; (b) derivative dQ/dV curves for the first and fifth cycle.
Reduction Electrochemical Behavior. The electrochemical performances of single-phase Li$_3$Ru$_y$Nb$_{1-y}$O$_4$ compounds were tested versus Li in Swagelok cells that were cycled in a galvanostatic mode at a C/10 rate starting either on oxidation or reduction. Figure 6 shows the cycling performances of cells started on reduction. Cutoff voltages were fixed above 1 V to limit conversion reaction. All of them, with the exception of Li$_3$Ru$_{0.1}$Nb$_{0.9}$O$_4$, show interesting reversible capacities of 1.6 Li, 1.4 Li, 0.8 Li, and 0.5 Li for cells containing Li$_3$RuO$_4$, Li$_3$Ru$_{0.7}$Nb$_{0.3}$O$_4$, Li$_3$Ru$_{0.5}$Nb$_{0.5}$O$_4$, and Li$_3$Ru$_{0.3}$Nb$_{0.7}$O$_4$, respectively. This decrease in capacity with increasing Nb content is indicative of its electrochemical transparency. In addition, for most compositions, except for Li$_3$RuO$_4$, the reduction occurs via two processes of similar capacity and with a number of Li exchanged during each process equal to the ruthenium content. This is well illustrated with Li$_3$Ru$_{0.7}$Nb$_{0.3}$O$_4$, which uptakes 0.7 Li atoms on the first process and 0.7 on the second one, suggesting that the two plateaus are associated with the reduction of Ru$^{5+}$ to Ru$^{4+}$ and of Ru$^{4+}$ to Ru$^{3+}$, respectively. These two redox processes are also confirmed by the corresponding derivative $dQ/dV$ plots in Figure 6b. Moreover, the $dQ/dV$ plots show a broadening of the peaks between the first and fifth cycles, which is more pronounced for the Ru-rich samples and indicative of Li-driven structural modifications. To better understand the science underpinning these electrochemical properties, in situ XRD measurements were performed.

Structure Evolution during Reduction. The lithiation–delithiation mechanism in Li$_3$RuO$_4$ was first examined by in situ XRD. During the cell discharge, we initially observe (Figure 7) a progressive disappearance of the pristine phase to the expense of a new one, which becomes pure at $x = 1$ (Li$_4$RuO$_4$). Upon further Li insertion, this new phase disappears and a new one is formed, and becomes a single phase at $x = 1.6$ (Li$_{4.6}$RuO$_4$). The two reduced phases Li$_4$RuO$_4$ and Li$_{4.6}$RuO$_4$ were both indexed with the same space group ($P2_1/a$) as the pristine phase but with increased lattice parameters ($a = 5.25$ Å, $b = 5.99$ Å, $c = 5.41$ Å, and $\beta = 113.66^\circ$) and ($a = 5.46$ Å, $b = 6.19$ Å, $c = 5.06$ Å, and $\beta = 90.58^\circ$), respectively. The strong decrease in the $\beta$ angle corresponds to a change in the oxygen stacking from ABCABC (O3 type) to ABAB. Since all octahedral positions are occupied in pristine Li$_3$RuO$_4$, the additional Li ions in the reduced compounds likely reside in tetrahedral positions. Combined X-ray and neutron refinements indicate that the Li$_{4.6}$RuO$_4$ structure consists in a T1-layered structure, in which extra Li occupies tetrahedral positions, while maintaining chains of Li and Ru in the metal layer (Figure S8 and Table S6 in the Supporting Information). Upon subsequent oxidation, the structural sequence proceeds with the pristine phase being fully recovered at the end of charge. However, a few peaks do...
not recover their full initial intensity, which is most likely related to the emergence of staking faults associated with the gliding of the transition-metal layers upon transformation from the O3 structure in the pristine phase to the T1 structure of the fully reduced Li4.6RuO4 phase. Note that the derivative curve for this sample shows a single peak in reduction while two are expected due to the two biphasic processes. Such a situation is not unique and has been found in other compounds (e.g., LiVPO4F or NaFePO4).26

The structural consequences of the Li insertion into Li3Ru0.7Nb0.3O4, Li3Ru0.5Nb0.5O4, and Li3Ru0.3Nb0.7O4 were investigated by in situ XRD (Figure S9 in the Supporting Information, Figure 8, and Figure 9, respectively). Although their structures differ, the insertion processes proceed alike: there is first an expansion of the unit cell when Ru5+ is reduced to Ru4+, followed by a distortion of the unit cell when Ru4+ is reduced to Ru3+. For Li3Ru0.5Nb0.5O4, the two reduction processes occur via solid-solution mechanisms (Figure 8). The first reduced phase Li3.5Ru0.5Nb0.5O4 was refined in the same space group P4122 as the parent phase with the following lattice parameters: a = 5.9744(5) Å and c = 8.5302(7) Å giving a cell volume of 76.12 Å3 per formula unit. In contrast, the fully reduced Li3.8Ru0.5Nb0.5O4 phase could only be refined considering a monoclinic distortion from P4122 to a P1121 space group with a = 6.077(1) Å, b = 6.020(2) Å, c = 8.857(2) Å, γ = 95.255(19)°, and a cell volume of 84.49 Å3 per unit formula. Because of the peculiar peak shape and broadening of some
reflections, we could not refine O or Li positions. Nevertheless, in light of our previous finding for the fully reduced Li$_3$RuO$_4$ phase—namely, the presence of Li$^+$ in tetrahedral sites—it is very likely that the same occurs for the fully reduced Li$_3$Ru$_{0.7}$Nb$_{0.3}$O$_4$ and Li$_3$Ru$_{0.5}$Nb$_{0.5}$O$_4$ phases. Therefore, we propose a model in which some octahedral sites of the pristine structure are emptied to place twice the number of Li in tetrahedral sites (see Figure 8 and Table S7 in the Supporting Information). The choice of the occupied tetrahedral site has been done using bond valence energy landscape approaches.

Overall, all members of the Li$_3$Ru$_y$Nb$_{1-y}$O$_4$ family react reversibly toward Li$^+/Li^0$ via two processes of nearly equal amplitude and with the total amount of inserted Li scaling with the number of Ru. Barely any activity could be detected from the Li$_3$Ru$_{0.1}$Nb$_{0.9}$O$_4$ sample, which suffers from kinetic issues, because of its poor electronic conduction.

### Electrochemistry upon Oxidation

We next address the electrochemical performances of the Li$_3$Ru$_y$Nb$_{1-y}$O$_4$ series on oxidation. The data obtained by cycling the cells at a rate of C/10 between 4 and 1.5 V are presented in Figure 10a. Remarkably, nearly 3 Li$^+$ are extracted at $\sim$4.1 V from Li$_3$Ru$_{0.5}$Nb$_{0.5}$O$_4$, but the discharge profile drastically differs from the charge profile, implying a pronounced modification of the material. The same trend is repeated for the other members, but with the amount of Li$^+$ removed from the 4 V plateau decreasing as the Nb substitution increases. Upon cycling, as exemplified in Figures 10b and 10c, the capacity decay, together with the charge–discharge curves becoming featureless, are indicative of a strong material evolution upon cycling. This was confirmed by in situ X-ray diffraction (Figure S10 in the Supporting Information), which indicates that, for all compositions, the material becomes amorphous during the first oxidation process and remains as such upon subsequent cycling. Lastly, since neither of the Ru$^{5+}$ or Nb$^{5+}$ ions are expected to be oxidized, the charge compensation mechanism associated with the removal of Li$^+$ must involve the anionic network and the oxygen redox process. To check this point, partially charged samples were investigated by XPS analysis. Focusing on the O 1s spectrum, we note the appearance of an extra component at 530.5 eV for the oxidized samples that we previously assigned to peroxy-like species (Figure S11 in the Supporting Information). In addition, gas pressure measurements reveal the release of gases through the oxidation process, which could be correlated to the observed amorphization (see Figure S12 in the Supporting Information). Taken together, these various aspects illustrate the complexity of the delithiation process in these compounds, hence justifying a full study by itself, which is beyond the scope of this paper, but will be the main topic of a forthcoming publication.

### DISCUSSION

In this report, we explored the Li$_3$Ru$_y$Nb$_{1-y}$O$_4$ phase diagram and demonstrate the existence of four different phases corresponding to $y = 1, 0.7, 0.5, 0.3$, and $0.1$, which exhibit an amphoteric behavior, with respect to lithium, since they can be either reduced via a classical Ru$^{5+} \rightarrow$ Ru$^{4+} \rightarrow$ Ru$^{3+}$ process, while Nb was found to remain electrochemically inactive, or oxidized by enlisting the participation of the anionic network. These results are now discussed with the hope to rationalize the phase evolution and the emergence of defects in the Li$_3$Ru$_y$Nb$_{1-y}$O$_4$ series, and to establish a relationship between structural and electrochemical properties.

To get more insight into the structural evolution in the series, we analyzed the changes in the coordination environment of the transition-metal cations. The Nb$^{5+}$ cations, beside forming Nb–O bonds with greater ionicity than Ru–O bonds,
have a $d^0$ electronic configuration; hence, such cations are well-known for their tendency to occupy asymmetric coordination with pronounced off-center displacements.\textsuperscript{28} This property is typically associated with the second-order Jahn–Teller effect,\textsuperscript{29} and it is very robust in solid-solution type systems where the $d^0$ cations are intermixed with other non-$d^0$ cations,\textsuperscript{30} such as Ru$^{5+}$ in our case. To parametrize off-center displacements of the cations and the deformation of the O-shell around them, we calculated $\Delta M$ and $\Delta O$ mean square deviation of the interatomic distances ($d_i$) from the corresponding average values ($\langle d \rangle$) of M–O and O–O bonds, respectively, according to the equations detailed in the caption of Figure 11. We also analyzed the M–M distances and the O–O distances between O atoms forming the edges between two adjacent MO6 octahedra, together with their corresponding O–M–O angles. The evolution of these parameters in the system is illustrated in Figure 11. Note that the parameters are averaged here, since no ordering between ruthenium and niobium could be identified. Upon increasing the Nb substitution up to Li$_3$Ru$_{0.5}$Nb$_{0.5}$O$_4$, there are only minor systematic changes in the parameters, despite drastic changes in the crystal structures. The most notable variations are associated with the increase of M–M and O–O distances, which is expected since Nb$^{5+}$ (0.65 Å) is larger than Ru$^{4+}$ (0.56 Å). Further increases in the Nb content (y < 0.5) results in a rapid growth of the M–M distances, together with the closing of the O–M–O angles associated with an increase of electrostatic interaction, because of the larger number of Nb–O ionic bonds. Equally, $\Delta M$ increases significantly, as a result of the increase in the number of $d^0$ cations (Nb), which triggers greater cation off-center displacements. It also very interesting to note that large off-center cation displacements and octahedra deformations favor changes in the topology of the M–O units from continuous 1D chains to 0D tetrahedral units. Apparently, the resulting structures represent a fine balance between the electronic configuration of the transition-metal cations, their ionic radii, and the electrostatic interactions between the ions.

Further searching for a structural indicator to describe the Li$_3$Ru$_{0.5}$O$_4$, Li$_3$Ru$_{0.7}$Nb$_{0.3}$O$_4$-$\text{Li}_3$Ru$_{0.5}$Nb$_{0.5}$O$_4$ and Li$_3$Ru$_{0.7}$O$_4$ Nb$_{0.3}$O$_4$ structures, in the second coordination sphere, we recognized the presence of two different coordination blocks within the chains made of the 12 cation neighbors of Ru/Nb sites: 10 Li and 2 Ru/Nb (see Figure 12). These two coordinations can be viewed as enantiomers denoted R and S. Interestingly, we found that these two enantiomers can be used as “building blocks” to reconstruct the different Ru/Nb frameworks. The zigzag chains can be described as an alternation of the R and S blocks ([R–S]$_\infty$); the helical chains can be viewed as made up of only one type of blocks (i.e., either [R–R]$_\infty$ or [S–S]$_\infty$), and the jagged chains are based on a more-complex alternation sequence of the R and S fragments (i.e., [R–S–S–R–]$_\infty$). Within this approach, it is easy to recognize that the local cooperative variations in the

![Figure 11](image.png)

**Figure 11.** (a) M–M distance (M = Ru/Nb) in blue, O–O distance between O atoms forming the edge between two MO$_6$ in pink, and the O–M–O angle between these two O atoms and the metal center, in red, extracted from Rietveld refinement of the combined synchrotron/neutron diffraction patterns are plotted in function of the ruthenium content. The O–O distortion coefficient, which is calculated using the formula $\Delta O = \frac{1}{\langle d \rangle} \sum (d_i - \langle d \rangle)^2$, where $d_i$ represents the individual O–O distances and $\langle d \rangle$ is the average distance, is shown in green and is also plotted as a function of the ruthenium content. The M–O distortion coefficient calculated with the formula $\Delta M = \frac{1}{\langle d \rangle} \sum (d_i - \langle d \rangle)^2$, where $d_i$ is the individual M–O distances and $\langle d \rangle$ is the average distance, is shown in pink. (b) Schematics showing the evolution of the local environment between two M atoms (M = Ru/Nb) (blue arrows represent the M–M distance, pink arrows represent the O–O distance between O atoms forming the edge between two MO$_6$, and red dashed curve represents the O–M–O angle between these two O atoms and the metal center).

![Figure 12](image.png)

**Figure 12.** Schematics presenting the “building blocks” in the structures. On the top part, the two blocks are made of a central M atom (M = Ru/Nb) surrounded by the 12 cations forming its 2nd coordination shell (10 Li and 2 M). In the middle part, the assembly leading to the different Li$_3$Ru$_{x}$Nb$_{1-x}$O$_4$ structures is illustrated. To assemble two blocks, one should merge the M–M bonds from one block to another. On the bottom of the figure, the resulting M–M frameworks are presented.
cation ordering that we observe in HAADF-STEM images (Figures 3e and 4d) can be described as inclusions of fragments or short-ordered sections of the R/S blocks violating the main sequence. It also indicates that, despite clear structural differences, 1D octahedral chains with different R/S sequences are rather close in energy. The feasibility to describe these structures as sequences of small unit blocks opens the door toward rationalization of the cation ordering as it has been done in other types of compounds, in which building blocks are more defined such as zeolites\(^{31}\) or metal organic frameworks,\(^{32}\) hence, a new playground to envision new structural packings that remain to be synthesized.

Considering the \(\text{Li}_1\text{Ru}_{0.1}\text{Nb}_{0.9}\text{O}_4\) structure built upon \((\text{MO})_4\) tetrahedral units, we should emphasize that we could not spot any intergrowth defects with domains containing 1D octahedral chains. This suggests significant difference in the stabilization energies of cluster against chain-type structures. This is consistent with the difference in the topology of the 1D chains and the 0D tetrahedral units, where each MO\(_6\) octahedron is connected to 2 and 3 MO\(_6\) octahedra, respectively. Clearly, the formation of the APBs in Li\(_3\)Ru\(_{1}\)Nb\(_{0.9}\)O\(_4\) is associated with the presence of small amount of Ru\(^{5+}\) cations and can be attributed to the difference in the coordination preferences of the Nb\(^{5+}\) and Ru\(^{5+}\) cations. However, the exact reason for the preferential formation of antiphase domains is still an open question that can be probably addressed using density functional theory (DFT) calculations.

Lastly, all the reported members, with the exception of Li\(_3\)Ru\(_{1}\)y Nb\(_{0.9}\)O\(_4\) because of its insulating behavior, have shown an electrochemical activity toward Li\(^+\)/Li, with the Li\(^+\) uptake/release scaling with the amount of Ru per unit formula. Upon oxidation, three Li ions can be removed from Li\(_3\)RuO\(_6\) and the capacity rapidly decays upon cycling. The main reason is nested in the instability of the Li\(_3\)RuO\(_4\) phase toward the Li\(^+\)/Li process, accompanied by the appearance of tetrahedral Li sites and structural distortions for the Ru\(^{4+}/\text{Ru}^{3+}\) process.

## CONCLUSIONS

In summary, we unveiled the synthesis and crystal chemistry of the Li\(_1\)Ru\(_{1}\)y Nb\(_{0.9}\)O\(_4\) system, which presents single phases for composition \(y = 1\), \((0.7−0.5)\), \(0.3\), \((0.1−0)\) that crystallize in a rocksalt structure, adopting four different cation ordering patterns and containing numerous defects as determined by combined SXRD, NPD, and TEM experiments. The feasibility to reconstruct these structures from simple “building blocks”, together with simulation, should enable us to grasp further light into the occurring structural changes as a function of the Ru/Nb content but also to predict new phases in this rich Li\(_3\)MO\(_4\) family (M = Nb, Ta, Sb,...). We also showed that these compounds present a rich electrochemistry upon oxidation enabling the removal of large amount of Li\(^+\) through a very complex charge compensation mechanism. The problem being identified, it now remains to engineer the stability of the oxidized “MO\(_4\)” phase via chemical substitution to fully capitalize the rich electrochemistry that they offer, bearing in mind the constraint of abundant elements.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.7b01511.

Crystallographic data for Li\(_3\)NbO\(_4\) (CIF)
Crystallographic data for Li\(_3\)Ru\(_{0.1}\)Nb\(_{0.9}\)O\(_4\) (CIF)
Crystallographic data for Li\(_3\)Ru\(_{0.7}\)Nb\(_{0.3}\)O\(_4\) (CIF)
Crystallographic data for Li\(_3\)Ru\(_{0.5}\)Nb\(_{0.5}\)O\(_4\) (CIF)
Crystallographic data for Li\(_3\)Ru\(_{0.1}\)O\(_4\) (CIF)
Additional Rietveld refinements, TEM data, and preliminary XPS and gas analysis data (PDF)

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### Notes

The authors declare no competing financial interest.

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