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# Metastable Layered Lithium-rich Niobium and Tantalum Oxides via Nearly Instantaneous Cation Exchange

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## Abstract

Lithium-rich early transition metal oxides are the source of excess removeable lithium that affords high energy density to lithium-rich battery cathodes. They are also candidates for solid electrolytes in all-solid-state batteries. These highly ionic compounds are sparse on phase diagrams of thermodynamically stable oxides, but soft chemical routes offer an alternative to explore new alkali-rich crystal chemistries. In this work, a new layered polymorph of  $\text{Li}_3\text{NbO}_4$  with coplanar  $[\text{Nb}_4\text{O}_{16}]^{12-}$  clusters is discovered through ion exchange chemistry. A more detailed study of the ion exchange reaction reveals that it takes place almost instantaneously, changing crystal volume by more than 22% within seconds. The transformation of coplanar  $[\text{Nb}_4\text{O}_{16}]^{12-}$  in  $\text{L-Li}_3\text{NbO}_4$  into the supertetrahedral  $[\text{Nb}_4\text{O}_{16}]^{12-}$  clusters found in the stable cubic  $\text{c-Li}_3\text{NbO}_4$  is also explored. Furthermore, this synthetic pathway is extended to access a new layered polymorph of  $\text{Li}_3\text{TaO}_4$ . NMR crystallography with  $^6,^7\text{Li}$ ,  $^{23}\text{Na}$ , and  $^{93}\text{Nb}$  NMR, X-ray diffraction, neutron diffraction, and first-principles calculations is applied to  $A_3\text{MO}_4$  ( $A = \text{Li, Na}$ ;  $M = \text{Nb, Ta}$ ) to identify local and long-range atomic structure, to monitor the unusually rapid reaction progression, and to track the phase transitions from the metastable layered phases to the known compounds found by high-temperature synthesis. A mechanism is proposed whereby some sodium is retained at short reaction times, which then undergoes proton exchange during water washing, forming a phase with hydrogen bonds bridging the coplanar  $[\text{Nb}_4\text{O}_{16}]^{12-}$  clusters. This study has implications for lithium-rich transition metal oxides and associated battery materials and for ion exchange chemistry in non-framework structures. The role of techniques that can detect light elements, local structure, and subtle structural changes in soft-chemical synthesis is emphasized.

## Introduction

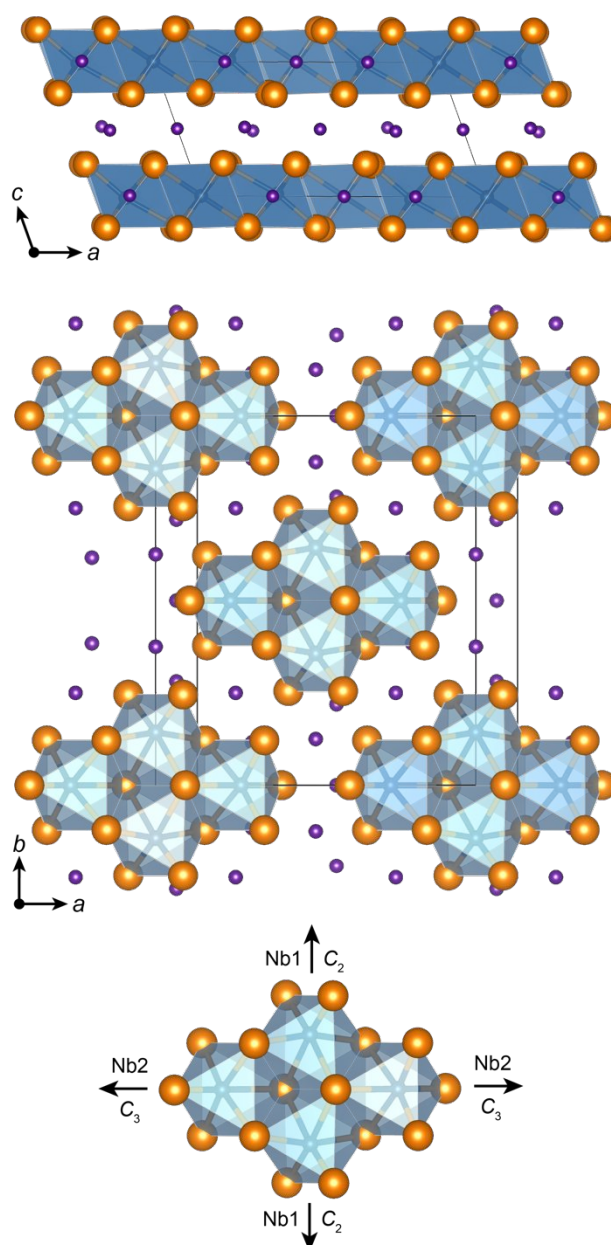
Lithium-rich compounds, oxides specifically, are emerging candidates for high-capacity lithium-ion battery electrode<sup>1–7</sup> materials. On the cathode side, there are many examples of lithium-rich structures with compositions that fall on a tie-line intermediate between a lithium stoichiometric mid-to-late transition metal oxide ( $\text{LiMO}_2$ ;  $M = \text{Ni}^{3+}$ ,  $\text{Co}^{3+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Fe}^{3+}$ ) and a lithium-rich early transition metal oxide ( $\text{Li}_2M^{4+}\text{O}_3$ ,  $\text{Li}_3M^{5+}\text{O}_4$ ,  $\text{Li}_4M^{6+}\text{O}_5$ ;  $M = \text{Ti}^{4+}$ ,  $\text{V}^{5+}$ ,  $\text{Nb}^{5+}$ ,  $\text{Mo}^{6+}$ ).<sup>5,8</sup> Though fewer, there are also lithium-rich high-rate anodes such as  $\text{Li}_3\text{V}_2\text{O}_5$  and  $\text{Li}_3\text{Nb}_2\text{O}_5$ .<sup>6,7</sup> The structural phase-space of lithium-rich transition metal oxides, however, is relatively narrow. Most known phases feature a close-packed oxygen sublattice with octahedral cations yielding the disordered rocksalt structure (*e.g.*, aforementioned compositions, hydrothermal  $\text{Li}_3\text{NbO}_4$  and  $\text{Li}_3\text{TaO}_4$ )<sup>8,9</sup> or a cation-ordered rocksalt superstructure (*e.g.*,  $\beta$ - $\text{Li}_2\text{TiO}_3$ ,  $\text{Li}_2\text{ZrO}_3$ ,  $c$ - $\text{Li}_3\text{NbO}_4$ ,  $\alpha$ - and  $\beta$ - $\text{Li}_3\text{TaO}_4$ ,  $\text{Li}_4\text{MoO}_5$ ,  $\text{Li}_4\text{WO}_5$ )<sup>10–14</sup>.

The known phase of  $\text{Li}_3\text{NbO}_4$  (cubic,  $\bar{I}43m$ , ICSD 75264), here denoted  $c$ - $\text{Li}_3\text{NbO}_4$  for reasons that will become apparent, has an interesting crystal structure comprising octahedral  $\text{NbO}_6$  that arrange in supertetrahedral clusters of  $[\text{Nb}_4\text{O}_{16}]^{12-}$ .<sup>12,13</sup>  $\text{Na}_3\text{NbO}_4$  (monoclinic,  $C2/m$ , ICSD 6116) also contains  $[\text{Nb}_4\text{O}_{16}]^{12-}$  clusters, however, in this case they are co-planar.<sup>15–17</sup> The unique arrangement of octahedral  $\text{NbO}_6$  in  $\text{Na}_3\text{NbO}_4$  thus gives rise to a layered compound that is denoted  $L$ - $\text{Na}_3\text{NbO}_4$ . Moreover, unlike most of the lithium compounds, it does not feature a close-packed oxygen sublattice. A related situation arises in the  $A_3\text{TaO}_4$  ( $A = \text{Li}$ ,  $\text{Na}$ ). There are two known high-temperature forms of  $\text{Li}_3\text{TaO}_4$ , the  $\alpha$  and  $\beta$  polymorphs, both featuring chains of  $\text{TaO}_6$  octahedra in a lattice of close-packed oxygen.<sup>18–20</sup>  $\text{Na}_3\text{TaO}_4$  is isostructural with  $\text{Na}_3\text{NbO}_4$ .<sup>14,21</sup>

In the context of exploratory synthesis toward materials relevant for next-generation batteries, it is worthwhile to pursue lithium-rich transition metal oxides with unique underlying crystal structures. Ion exchange has been successfully applied as a synthetic route to create a variety of new or low-defect lithium metal oxides.<sup>22–27</sup> The mild conditions of ion exchange, relative to high-temperature ceramic methods, favor topotactic reactions that lead to metastable products with complete or systematic partial replacement<sup>28</sup> of the original guest cations. Typical host structures are interconnected frameworks or 2D layered solids. Of the non-interconnected hosts that undergo ion exchange, polyoxometalates (POMs) with large, well-

defined cluster anions are perhaps the best known.<sup>29</sup> Less explored is the chemistry of small clusters found among the alkali-rich early transition metal oxides.

In this work, we synthesized layered L-Li<sub>3</sub>NbO<sub>4</sub> with zero-dimensional (0D) coplanar [Nb<sub>4</sub>O<sub>16</sub>]<sup>12-</sup> anionic clusters and a non-close-packed oxygen sublattice via cation exchange in a molten salt flux. An NMR crystallography approach combining X-ray and neutron diffraction, <sup>6</sup>Li, <sup>7</sup>Li, <sup>23</sup>Na, and <sup>93</sup>Nb solid-state NMR, and *ab initio* structure and spectral calculations was adopted to characterize L-Li<sub>3</sub>NbO<sub>4</sub> and its relationship to related phases such as c-Li<sub>3</sub>NbO<sub>4</sub> and L-Na<sub>3</sub>NbO<sub>4</sub>. The combination of experimental and computational solid-state NMR spectra is particularly powerful here owing to the global symmetry and local distortion differences amongst the various phases. After discovering that the ion exchange reaction to form L-Li<sub>3</sub>NbO<sub>4</sub> occurs in a matter of seconds, diffraction, NMR, and DFT were again combined to track the composition and structure evolution and the ion exchange mechanism as a function of reaction time. Finally, we show that this synthetic and characterization methodology are transferrable through the realization of another new phase, layered L-Li<sub>3</sub>TaO<sub>4</sub>.



**Figure 1.** Crystal structure of layered Li<sub>3</sub>NbO<sub>4</sub> synthesized topotactically from Na<sub>3</sub>NbO<sub>4</sub>. Planar [Nb<sub>4</sub>O<sub>16</sub>]<sup>12-</sup> clusters align in the *ab* plane and are separated by a sea of alkali cations. The bottom panel depicts the direction and symmetry of the SOJT distortions of niobium atoms within their respective octahedra. Lithium atoms in purple, NbO<sub>6</sub> octahedra in blue, and oxygen atoms in orange.

## Experimental

**Reagents and synthesis.** The stable high-temperature phases of  $\text{L-Na}_3\text{NbO}_4$ ,  $\text{L-Na}_3\text{TaO}_4$ ,  $\text{c-Li}_3\text{NbO}_4$ , and  $\text{m-Li}_3\text{TaO}_4$  were synthesized in approximately 1 g batches according to previously reported high-temperature solid-state methods.<sup>30,15</sup>  $\text{T-Nb}_2\text{O}_5$  (99.85%,  $D_{50} = 450$  nm, CBMM) or  $\text{L-Ta}_2\text{O}_5$  (99.9%, MSE Supplies) were ground with  $\text{Li}_2\text{CO}_3$  (anhydrous,  $\geq 99.0\%$ , Sigma Aldrich) or  $\text{Na}_2\text{CO}_3$  (anhydrous, 99.95%, Sigma Aldrich) in stoichiometric amounts with a mortar and pestle and pressed into a pellet at 300 MPa with a 13-mm-diameter stainless steel die. The pellet was heated in a magnesia crucible with a magnesia cover at 850 °C for 12 hours for the sodium compounds or 1000 °C for 12 hours for the lithium compounds. Ion exchange from  $\text{L-Na}_3\text{MO}_4$  to  $\text{L-Li}_3\text{MO}_4$  ( $M = \text{Nb, Ta}$ ) was performed by grinding together 200 mg of the layered sodium compound with  $\text{LiNO}_3$  ( $\geq 98.5\%$ , Sigma Aldrich) in a 1:10  $\text{Na}_3\text{MO}_4$ :salt mass ratio. The mixture was heated in an alumina crucible at 335 °C for up to 12 h. After heating, the salt was dissolved with DI water and the final product was recovered by vacuum filtration over a PVDF membrane (Durapore, 0.22  $\mu\text{m}$ , hydrophilic). For the time-stepped ion exchange, the salt was pre-heated to 335 °C before  $\text{L-Na}_3\text{NbO}_4$  was added into the molten salt inside the crucible. The sample and flux reacted for variable times ranging from 30 seconds to 12 hours before being quenched in cold water.

**Powder X-ray diffraction (PXRD) and scanning electron microscopy (SEM).** Powder X-ray diffraction was performed with a Bruker D8 Advance powder diffractometer using  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54$  Å) with operating voltage of 40 kV and a current of 40 mA. X-ray diffraction powder patterns were recorded from 5–90°  $2\theta$  with a step size of 0.020° at 0.4 seconds per step. Scanning electron microscopy was performed with an FEI Apreo SEM operating with a beam current of 0.40 nA and a voltage of 10 kV.

**Neutron powder diffraction.** Time-of-flight neutron powder diffraction (TOF-NPD) data were measured on the POWGEN diffractometer at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory.<sup>31</sup> The neutron samples comprised 4.242 g of  $\text{L-Na}_3\text{NbO}_4$  loaded into an 8-mm-diameter cylindrical vanadium can and 1.923 g of  $\text{Li}_3\text{NbO}_4$  loaded into a 6-mm-diameter cylindrical vanadium can. Both cans were loaded into the POWGEN sample changer (PAC) and measured at 20 K and 300 K. Data were collected on POWGEN detector bank 1 with a center wavelength of 0.8 Å ( $d$ -spacing range 0.1–8 Å) for  $\text{Li}_3\text{NbO}_4$  at 20 K and detector bank 2 with a center wavelength of 1.5 Å ( $d$ -spacing range 0.5–12.5 Å) for all other measurements. Data collection times for  $\text{L-Na}_3\text{NbO}_4$  at 20 K,  $\text{L-Na}_3\text{NbO}_4$  at 300 K,  $\text{L-Li}_3\text{NbO}_4$

at 20 K, and L-Li<sub>3</sub>NbO<sub>4</sub> at 300 K were 44, 86, 150, and 58 mins, respectively. Rietveld refinements were performed in GSAS-II.<sup>32</sup> The large sample of L-Na<sub>3</sub>NbO<sub>4</sub> prepared for neutron diffraction contained 1 wt.% Na<sub>2</sub>CO<sub>3</sub> while the L-Li<sub>3</sub>NbO<sub>4</sub> sample contained 1 wt.% Li<sub>2</sub>CO<sub>3</sub>; both could be observed by their characteristic (110) reflections at  $Q = 1.400 \text{ \AA}^{-1}$  and  $1.509 \text{ \AA}^{-1}$ , respectively. The neutron wavevector  $Q$  is defined as  $Q = 2\pi/d$ .

**Particle size analysis.** Particle size distributions were recorded with a Shimadzu SALD-7500nano particle size analyzer. Each powder was dispersed in isopropyl alcohol at a concentration of 1 mg/mL, sonicated, and measured in a quartz cell (Batch Cell SALD-BC75) with a 405 nm laser. The refractive indices for these measurements were calculated with methods by Kinoshita.<sup>33</sup>

**Solid-state NMR experiments.** All NMR measurements were performed at 9.4 T on a Bruker Ascend 400 magnet and Bruker Avance NEO NMR spectrometer with a 5.0 mm or 1.6 mm Phoenix HX probe. Samples were fully packed into zirconia rotors with PCTFE and polyimide (5 mm) or polyimide and polyamide-imide (1.6 mm) caps. 1D measurements used a direct pulse–acquire pulse sequence and a recycle delay time of  $\geq 5 \times T_1$ .  $T_1$  (longitudinal) relaxation was measured with a saturation-recovery pulse sequence with up to 37 delay times spanning 10  $\mu$ s up to 10,000 s, equally spaced in  $\log_{10}(t)$ .  $T_1$  relaxation data, recycle delays, and the number of FIDs recorded for each experiment are reported in Supplementary Information Figure S1, Table S1, and Table S2. NMR data processing and lineshape fits were performed with Bruker TopSpin 4.3.0 and DMfit.<sup>34</sup>

This work uses the Haeberlen convention for NMR tensors. With the principal components of the shift tensor ordered such that  $|\delta_{ZZ} - \delta_{iso}| \geq |\delta_{XX} - \delta_{iso}| \geq |\delta_{YY} - \delta_{iso}|$ , the isotropic shift  $\delta_{iso} = \frac{\delta_{XX} + \delta_{YY} + \delta_{ZZ}}{3}$ , chemical shift anisotropy  $\delta_{aniso} = \delta_{ZZ} - \delta_{iso}$ ; and the chemical shift asymmetry  $\eta_{CS} = \frac{\delta_{YY} - \delta_{XX}}{\delta_{ZZ} - \delta_{iso}}$ . The above definition of  $\delta_{aniso}$  is sometimes referred to as the reduced anisotropy, which is equal to 2/3 of the ‘full’ anisotropy  $\Delta\delta = \delta_{ZZ} - \frac{\delta_{XX} + \delta_{YY}}{2}$  used by some authors and programs. With the principal components of the electric field gradient (EFG) tensor at the nucleus ordered such that  $|V_{ZZ}| \geq |V_{YY}| \geq |V_{XX}|$ , the quadrupolar coupling constant  $C_Q$  is defined by the nuclear quadrupole moment  $Q$ , the largest principal component of the EFG  $V_{ZZ}$ , the electric charge  $e$ , and Planck’s constant  $h$  according to  $C_Q = \frac{eQ \cdot V_{ZZ}}{h}$ . The quadrupolar asymmetry parameter  $\eta_Q$  is defined as  $\eta_Q = \frac{V_{XX} - V_{YY}}{V_{ZZ}}$ . The relative orientations of the chemical

shift and quadrupolar tensors are defined by a set of Euler angles  $\alpha$ ,  $\beta$ ,  $\gamma$  defined here in the (ZYZ) Rose convention as implemented in MagresView 2.0.<sup>35</sup>

**<sup>6</sup>Li and <sup>7</sup>Li NMR.** <sup>6</sup>Li and <sup>7</sup>Li experiments were measured at Larmor frequencies of 58.88 and 155.51 MHz, respectively, with the sample rotated about the magic angle at a frequency of 10 or 20 kHz (no temperature regulation). For <sup>6</sup>Li, spectra were acquired using a 90° pulse of 6.25  $\mu$ s (40 kHz) in the 5 mm probe or 2.70  $\mu$ s (93 kHz) in the 1.6 mm probe. For <sup>7</sup>Li, spectra were acquired using a 90° pulse of 6.10  $\mu$ s (41 kHz) in the 5 mm probe or 2.15  $\mu$ s (116 kHz) in the 1.6 mm probe. Both <sup>6</sup>Li and <sup>7</sup>Li were referenced with respect to 9.7 m LiCl in D<sub>2</sub>O at 0 ppm.<sup>36</sup>

**<sup>23</sup>Na NMR.** <sup>23</sup>Na spectra were measured at the Larmor frequency of 105.84 MHz and 10 kHz (1D) or 12.5 kHz MAS (MQMAS). 1D spectra were acquired with a 45° pulse of 1.50  $\mu$ s (83 kHz). A three-pulse *z*-filtered MQMAS<sup>37</sup> experiment was conducted with 9  $\mu$ s, 3  $\mu$ s, and 28  $\mu$ s pulses. The MQMAS experiment used a recycle delay of 18 s, 96 FIDs per row, and 200 rows (96 h experimental time). <sup>23</sup>Na was referenced to solid NaCl at 7.21 ppm.<sup>38</sup> The MQMAS spectrum is referenced according to the Wimperis convention.<sup>39</sup>

**<sup>93</sup>Nb NMR.** <sup>93</sup>Nb spectra were measured at a Larmor frequency of 97.83 MHz under magic angle rotation at a frequency of 30 or 39 kHz. 1D spectra were acquired with a pulse of 0.4  $\mu$ s, which is estimated to be a 20° pulse based on the liquid 90° pulse of nearby <sup>13</sup>C. <sup>93</sup>Nb spectra of several samples were recorded with pulses varying from 0.25 to 0.75  $\mu$ s and the observed lineshapes were not sensitive to these variations. <sup>93</sup>Nb was referenced to solid LiNbO<sub>3</sub> at −1004 ppm (Supplementary Figure S2).<sup>40</sup>

## DFT Calculations

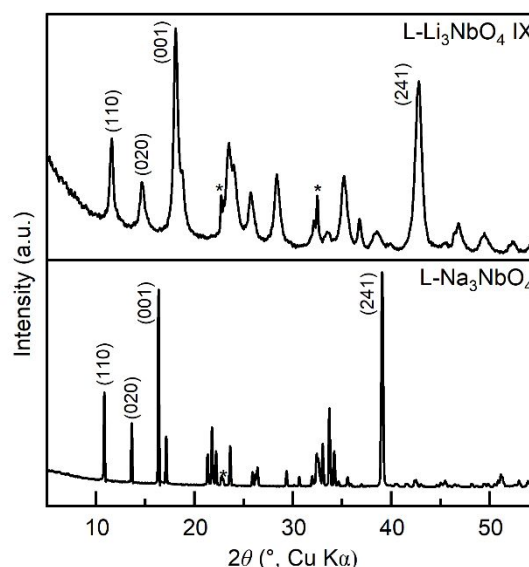
All structures reported in this work have been geometry optimised using forces and stresses derived from density-functional theory (DFT) calculations as implemented in the CASTEP v21 planewave DFT code.<sup>41</sup> NMR parameters were also calculated using CASTEP and the gauge-including projector augmented wave (GIPAW) method.<sup>42</sup> Calculations were performed using a Monkhorst–Pack<sup>43,44</sup> *k*-point grid with a spacing of  $2\pi \times 0.03 \text{ \AA}^{-1}$  and a planewave cut-off energy of 1000 eV. CASTEP's on-the-fly ultrasoft pseudopotentials from CASTEP v21 were used with the PBE<sup>12</sup> exchange–correlation functional as implemented in CASTEP.

## Results and Discussion

**Synthesis and structure.** Given the interesting relationship between the supertetrahedral  $[M_4O_{16}]^{12-}$  arrangement of octahedra in the stable cubic phase  $c\text{-Li}_3\text{NbO}_4$  and the coplanar  $[M_4O_{16}]^{12-}$  cluster of the stable layered phase  $\text{L-Na}_3\text{NbO}_4$ , we set out to explore whether the layered polymorph of  $\text{Li}_3\text{NbO}_4$  could be realized via ion exchange. Host structures capable of topotactic ion exchange typically feature 2D or 3D connectivity, so there was little precedence for the process in 0D cluster compounds such as  $\text{L-Na}_3\text{NbO}_4$ .

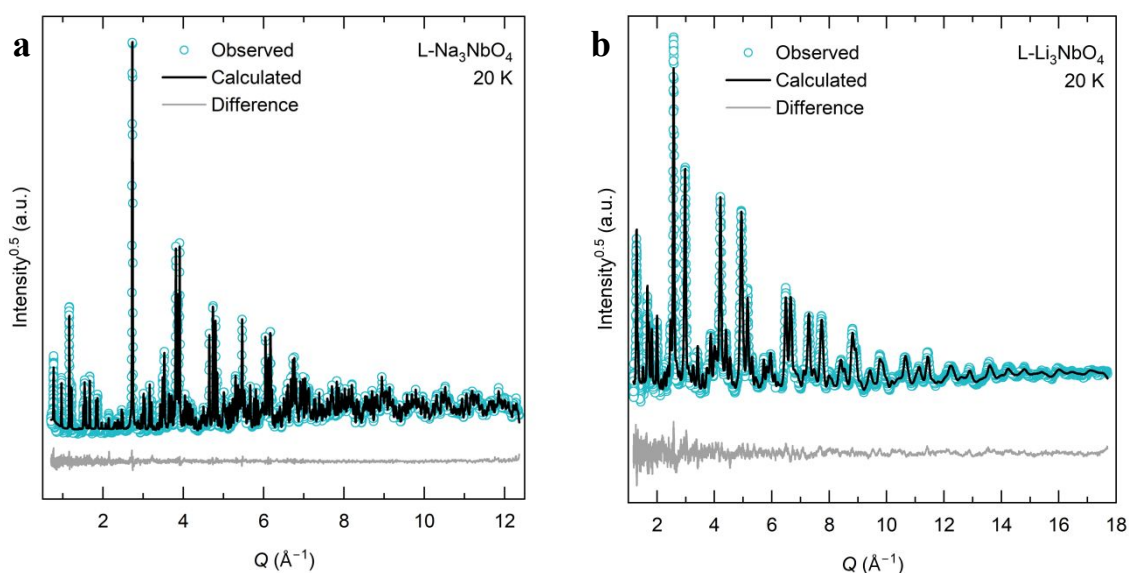
$\text{L-Na}_3\text{NbO}_4$  was prepared at  $850\text{ }^\circ\text{C}$  from  $\text{Nb}_2\text{O}_5$  and  $\text{Na}_2\text{CO}_3$ . The sample was phase pure with the exception of a small quantity of  $\text{NaNbO}_3$ , typically 2–3%, that could have formed during the synthesis or by reaction of the product with atmospheric carbon dioxide. In the initial ion exchange reaction,  $\text{L-Na}_3\text{NbO}_4$  was left in a flux of molten  $\text{LiNO}_3$  for 12 h. The diffraction peaks of the ion exchanged product, whilst substantially broadened, could be indexed in the same unit cell with lattice parameters  $a, b, c$  contracted by approximately 7%, 8%, and 10%, respectively (Figure 2).

Sodium and lithium are not easily differentiated by X-rays in a compound where the scattering is dominated by niobium so two additional characterization routes were pursued: neutron diffraction and solid-state NMR spectroscopy. Multigram samples of  $\text{L-Na}_3\text{NbO}_4$  and  $\text{L-Li}_3\text{NbO}_4$  were prepared and measured at 20 K and 300 K with time-of-flight neutron diffraction on the POWGEN beamline at Oak Ridge National Laboratory (Supplementary Information Figure S3). Rietveld refinement of  $\text{L-Na}_3\text{NbO}_4$  was carried out with 20 K and 300 K datasets, allowing the lattice parameters, atomic positions, and isotropic displacement parameters to refine freely (Figure 3a, Supplementary Information Figure S4). The results of these fits are given in Table 1 and as crystallographic information files in the Supplementary Information.  $\text{L-Na}_3\text{NbO}_4$  was used as the starting point for the refinement of  $\text{L-Li}_3\text{NbO}_4$ . First, the lattice parameters were adjusted by hand to roughly match the peak positions, which changed by too much during the ion exchange to be handled by unassisted least-squares refinement (Figures 2–3, Supplementary Information Figure S4). The room-temperature unit



**Figure 2.** X-ray diffraction patterns of layered  $\text{Na}_3\text{NbO}_4$  (bottom) and  $\text{Li}_3\text{NbO}_4$  after 12 h of ion exchange in a molten lithium salt (top). Some of the most prominent reflections are labeled. Asterisks denote observed  $\text{NaNbO}_3$  reflections.

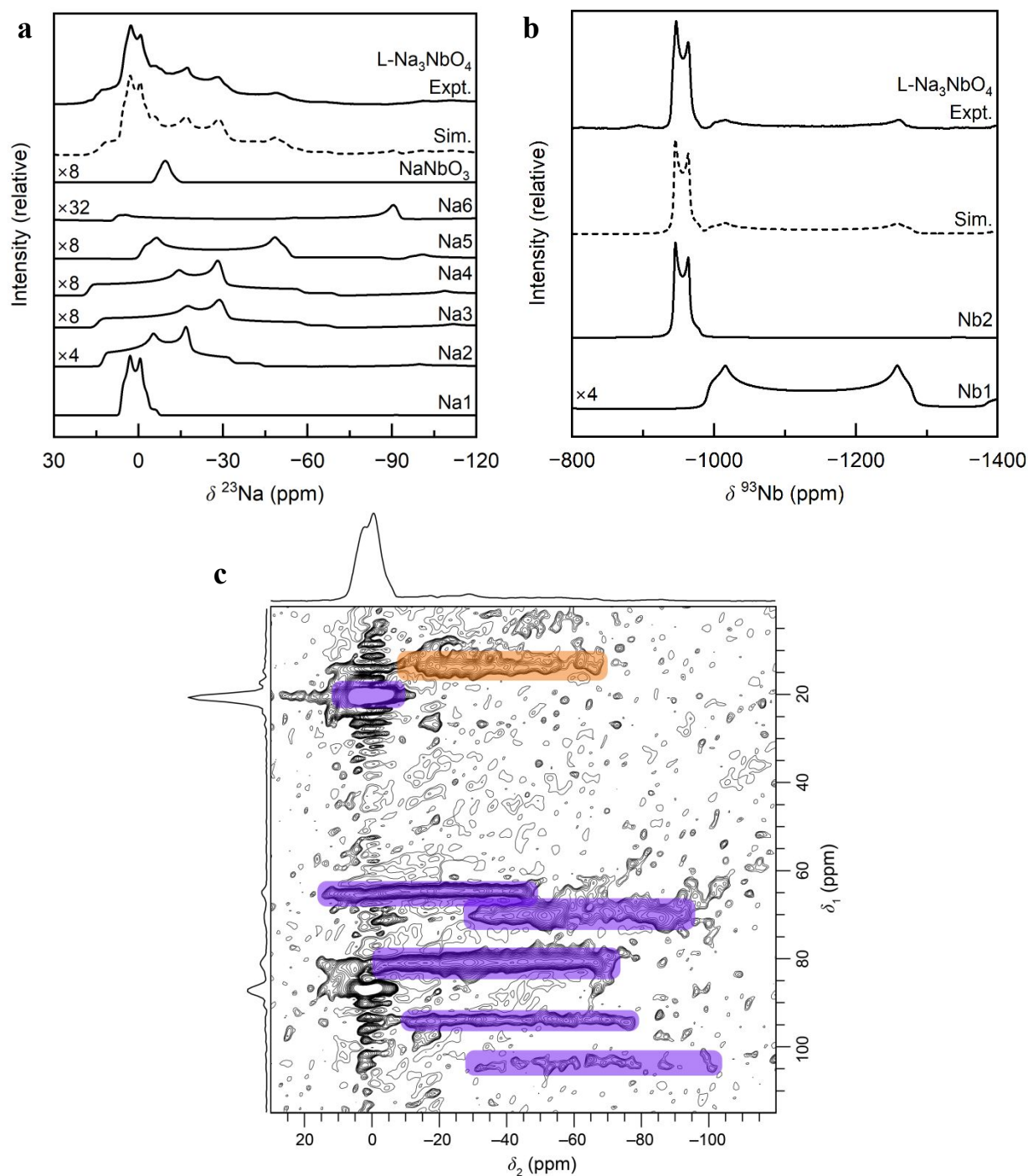
cell volume of  $\text{L-Na}_3\text{NbO}_4$  decreased by 22.6% upon ion exchange with lithium. Broadened line shapes, which likely come from strain<sup>45</sup> since the particle size did not change significantly during ion exchange (Supplementary Information Figures S5–S6), were accounted for in the refinement by the isotropic strain parameter and instrumental broadening terms. In the structure model of  $\text{L-Li}_3\text{NbO}_4$ , lithium ions were initially placed on the sodium positions of  $\text{L-Na}_3\text{NbO}_4$ . The positions were refined followed by constrained isotropic displacement parameter refinement (one  $B_{\text{iso}}$  per atomic species), which yielded a good fit to the data (Figure 3b, Supplementary Information Figure S4b). The presence of lithium was also supported by clearly defined pockets of negative nuclear density in Fourier difference maps when any one of the lithium atoms was removed. DFT geometry optimizations of  $\text{L-Na}_3\text{NbO}_4$  and  $\text{L-Li}_3\text{NbO}_4$  yielded close agreement with the experimental crystal structures (Table 1, Supplementary Table S3).



**Figure 3.** Neutron powder diffraction patterns and Rietveld refinement fits of (a)  $\text{L-Na}_3\text{NbO}_4$  and (b)  $\text{L-Li}_3\text{NbO}_4$ . Square-root intensity is shown to better depict data to high  $Q$ .

**Table 1.** Lattice parameters of  $\text{L-Na}_3\text{NbO}_4$  and  $\text{L-Li}_3\text{NbO}_4$  from refinement of the structures with neutron powder diffraction data.

Layered $C2/m$	300 K			20 K		
	$\text{Na}_3\text{NbO}_4$	$\text{Li}_3\text{NbO}_4$	$\Delta$ (%)	$\text{Na}_3\text{NbO}_4$	$\text{Li}_3\text{NbO}_4$	$\Delta$ (%)
$a$ (Å)	11.1218(4)	10.39(2)	−6.6	11.0923(5)	10.36(2)	−6.6
$b$ (Å)	13.00203(7)	11.944(3)	−8.1	12.9711(1)	11.904(3)	−8.2
$c$ (Å)	5.7529(1)	5.202(4)	−9.6	5.7350(2)	5.179(4)	−9.7
$\beta$ (°)	109.4905(6)	109.91(2)		109.4294(7)	109.83(2)	
Volume (Å <sup>3</sup> )	784.233(6)	606.7(1)	−22.6	778.16(2)	601.0(1)	−22.8



**Figure 4.** (a)  $^{23}\text{Na}$  1D, (b)  $^{93}\text{Nb}$  1D, and (c)  $^{23}\text{Na}$  MQMAS NMR of  $\text{L-Na}_3\text{NbO}_4$  at 9.4 T. The simulated  $^{23}\text{Na}$  spectrum in (a) includes contributions from the six unique sodium sites in the crystal structure and the  $\text{NaNbO}_3$  impurity. Broader sites in (a,b) are scaled up in intensity, as denoted, to better show their lineshapes. The purple boxes in (c) correspond to the six crystallographic sodium sites in  $\text{L-Na}_3\text{NbO}_4$  while the orange box corresponds to  $\text{NaNbO}_3$ .  $^{23}\text{Na}$  1D and MQMAS were measured at 10 and 12.5 kHz MAS, respectively, and  $^{93}\text{Nb}$  was measured at 38.5 kHz MAS.

Solid-state NMR spectroscopic analysis of the ion exchange reaction also started with  $\text{L-Na}_3\text{NbO}_4$ . The crystal structure of  $\text{L-Na}_3\text{NbO}_4$  features six sodium and two niobium atoms in the asymmetric unit.  $^{23}\text{Na}$  and  $^{93}\text{Nb}$  NMR of  $\text{L-Na}_3\text{NbO}_4$ , simulated with parameters refined

from planewave DFT calculations, give good agreement between experiment and theory (Figure 4, Tables 2–3). Measurement of  $^{23}\text{Na}$  NMR after the ion exchange process gives not only a quantitative measure of the extent of the ion exchange but also yields phase-specific information on the residual sodium. The only sodium remaining in the washed, ion-exchanged sample, L- $\text{Li}_3\text{NbO}_4$ , was the 2–3%  $\text{NaNbO}_3$  that was present in the original L- $\text{Na}_3\text{NbO}_4$  precursor (Figure 5a). This  $\text{NaNbO}_3$  is a mixture of two polymorphs, *Pbcm* and *P2<sub>1</sub>ma*, fit on the basis of the detailed work by Johnston et al.<sup>46</sup> (Table 2).  $\text{NaNbO}_3$  apparently does not undergo ion exchange in molten lithium nitrate within 12 h at 335 °C.

**Table 2.**  $^{23}\text{Na}$  NMR of  $\text{Na}_3\text{NbO}_4$  and  $\text{NaNbO}_3$ .

Table 1.  $^{23}\text{Na}$  NMR of  $\text{La}_3\text{NbO}_4$  and  $\text{NaNbO}_3$ .

	Site	calculated					experimental <sup>a</sup>		
		$\sigma_{\text{iso}}$ (ppm)	$\delta_{\text{aniso}}$ (ppm)	$\eta_{\text{CS}}$	$C_{\text{Q}}$ (MHz)	$\eta_{\text{Q}}$	$\delta_{\text{iso}}$ (ppm)	$C_{\text{Q}}$ (MHz)	$\eta_{\text{Q}}$
L- $\text{Na}_3\text{NbO}_4$	Na1	556.8	10.6	0.11	1.529	0.41	6.7(5)	1.55(10)	0.41(1)
	Na2	548.0	−22.6	0.79	−3.133	0.57	15(1)	3.1(2)	0.57(3)
	Na3	544.5	−14.0	0.32	−3.726	0.72	16(1)	3.7(2)	0.72(1)
	Na4	542.4	−11.1	0.92	−3.801	0.62	29(1)	3.8(2)	0.68(4)
	Na5	551.0	−8.5	0.55	−4.334	0.08	10(1)	4.2(2)	0.10(2)
	Na6	551.7	−35.0	0.35	5.668	0.62	9(5) <sup>b</sup>	5.5(5) <sup>b,c</sup>	n/a <sup>b,c</sup>
$\text{NaNbO}_3$	Na1						−1.3(5)	2.1(1)	0.01(5)
<i>Pbcm</i>	Na2						−5.7(5)	1.0(1)	0.8(2)
$\text{NaNbO}_3$	Na1						−2.1(5)	2.1(1)	0.9(1)
<i>P2<sub>1</sub>ma</i>	Na2						−5.5(5)	1.1(1)	0.7(2)

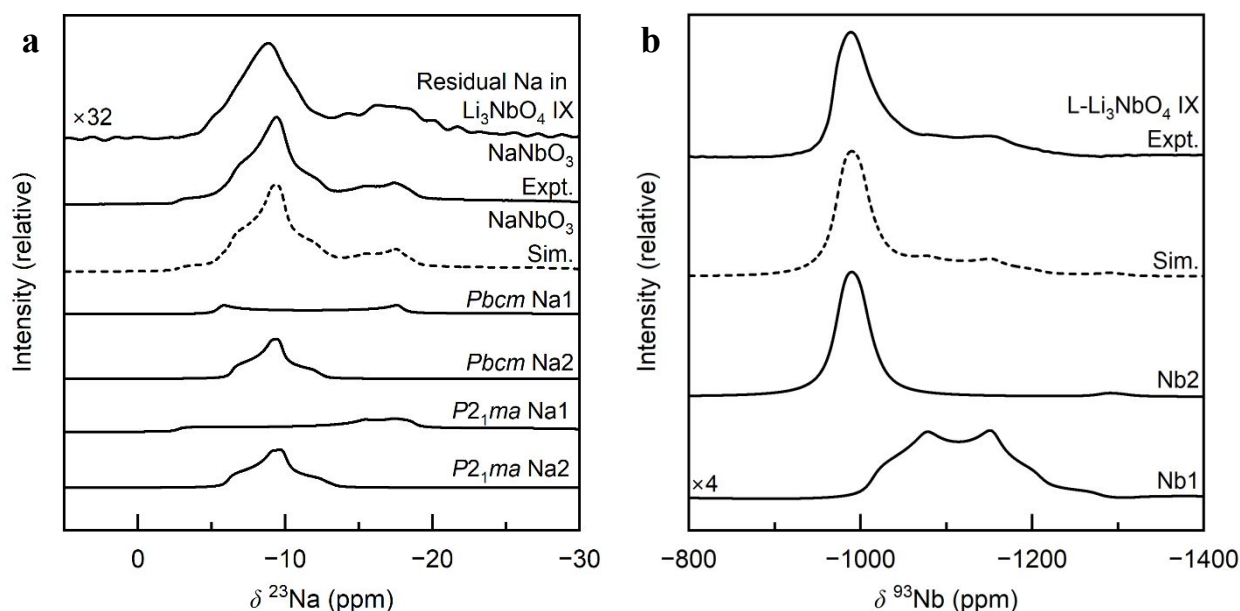
<sup>a</sup>‘Experimental’ values obtained by first simulating the GIPAW calculated values and then refining the isotropic chemical shift and the quadrupolar coupling magnitude and asymmetry to obtain a best-fit of the simulation to the experimental data. Error estimates are based on evaluation of the local minimum fit and do not exclude the possibility that this is not the global minimum fit given the degree of  $^{23}\text{Na}$  spectral overlap. <sup>b</sup>Determined from the  $\delta_{\text{I}} \sim 105$  ppm low-intensity site observed in the MQMAS spectrum. <sup>c</sup> $C_{\text{Q}}$  was calculated from  $P_{\text{Q}} = C_{\text{Q}}(1 + \eta_{\text{Q}}^2/3)^{1/2}$  using the GIPAW calculated value of  $\eta_{\text{Q}}$ .

**Table 3.**  $^{93}\text{Nb}$  NMR of  $\text{Li}_3\text{NbO}_4$  and  $\text{Na}_3\text{NbO}_4$ .

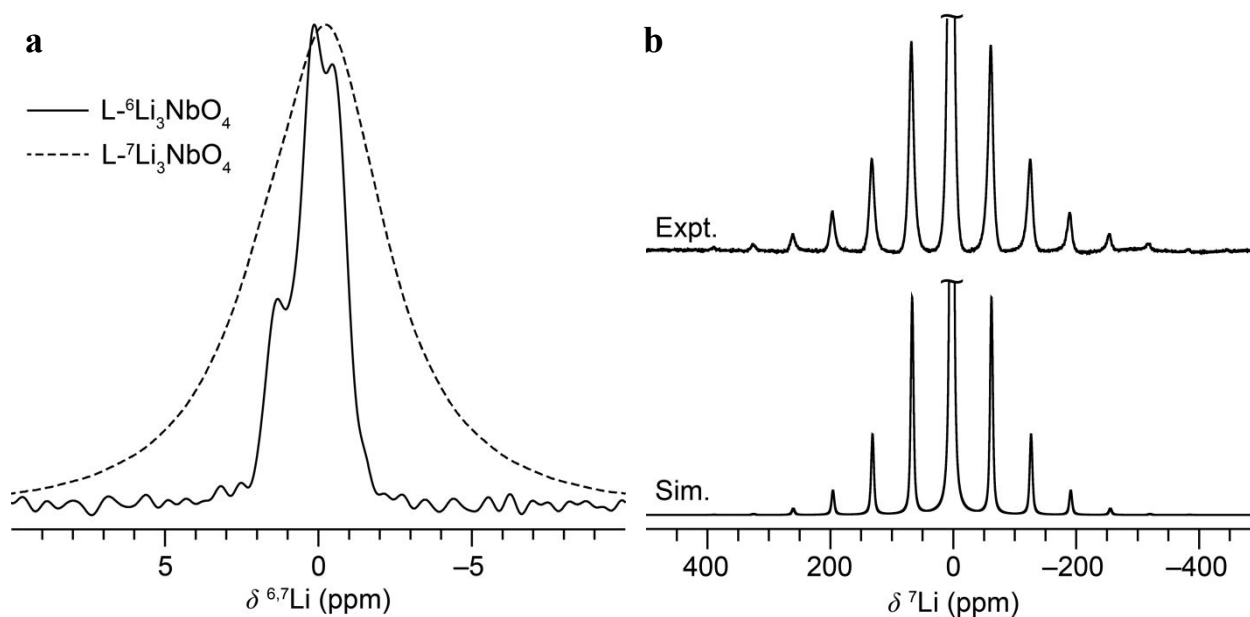
		<u>calculated</u>					<u>experimental<sup>a</sup></u>		
		Site	$\sigma_{iso}$ (ppm)	$\delta_{aniso}$ (ppm)	$\eta_{CS}$	$C_Q$ (MHz)	$\eta_Q$	$\delta_{iso}$ (ppm)	$C_Q$ (MHz)
c-	Nb1	313	−128	0.00	−13.2	0.00	−977(5)	12.4(2)	0.12(2)
Li <sub>3</sub> NbO <sub>4</sub>									
L-	Nb1	303	−129	0.28	27.3	0.41	−998(10)	27(2)	0.41(5)
Li <sub>3</sub> NbO <sub>4</sub>	Nb2	334	124	0.24	−11.9	0.08	−977(5)	12(2)	0.08(5)
L-	Nb1	223	−93	0.02	42.9	0.02	−924(10)	39.0(5)	0.08(3)
Na <sub>3</sub> NbO <sub>4</sub>	Nb2	247	108	0.51	17.4	0.00	−938(5)	10.9(2)	0.00(2)

<sup>a</sup>‘Experimental’ values obtained by first simulating the GIPAW calculated values and then refining the isotropic chemical shift and the quadrupolar coupling magnitude and asymmetry to obtain a best-fit of the simulation to the experimental data.

The <sup>93</sup>Nb MAS NMR spectrum of L-Li<sub>3</sub>NbO<sub>4</sub> is in good agreement with the parameters calculated from DFT on the basis of the structure refined from neutron diffraction data (Figure



**Figure 5.** (a) <sup>23</sup>Na and (b) <sup>93</sup>Nb NMR of L-Li<sub>3</sub>NbO<sub>4</sub> at 9.4 T. The simulated <sup>23</sup>Na spectrum is made up of two polymorphs of the NaNbO<sub>3</sub> impurity present in the precursor L-Na<sub>3</sub>NbO<sub>4</sub>. <sup>23</sup>Na was measured at 10 kHz MAS and <sup>93</sup>Nb was measured at 30 kHz MAS. The residual NaNbO<sub>3</sub> in (a) and the broader Nb2 site in (b) are scaled up in intensity, as denoted, to better show their lineshapes.

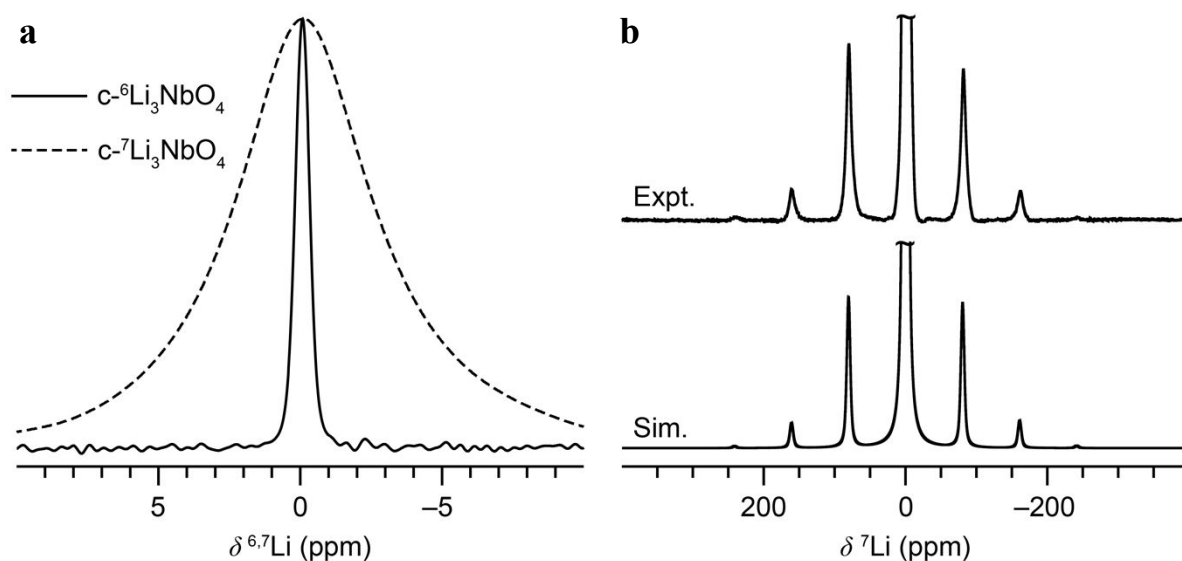


**Figure 6.** (a) <sup>6,7</sup>Li centerband spectra and (b) <sup>7</sup>Li spinning sideband manifold of L-Li<sub>3</sub>NbO<sub>4</sub> at 9.4 T and 10 kHz MAS. Spectra in (a) are intensity normalized. Centerband truncated in (b). Sideband simulation performed with the calculated <sup>7</sup>Li *C<sub>Q</sub>* and *η<sub>Q</sub>* parameters for L-Li<sub>3</sub>NbO<sub>4</sub>.

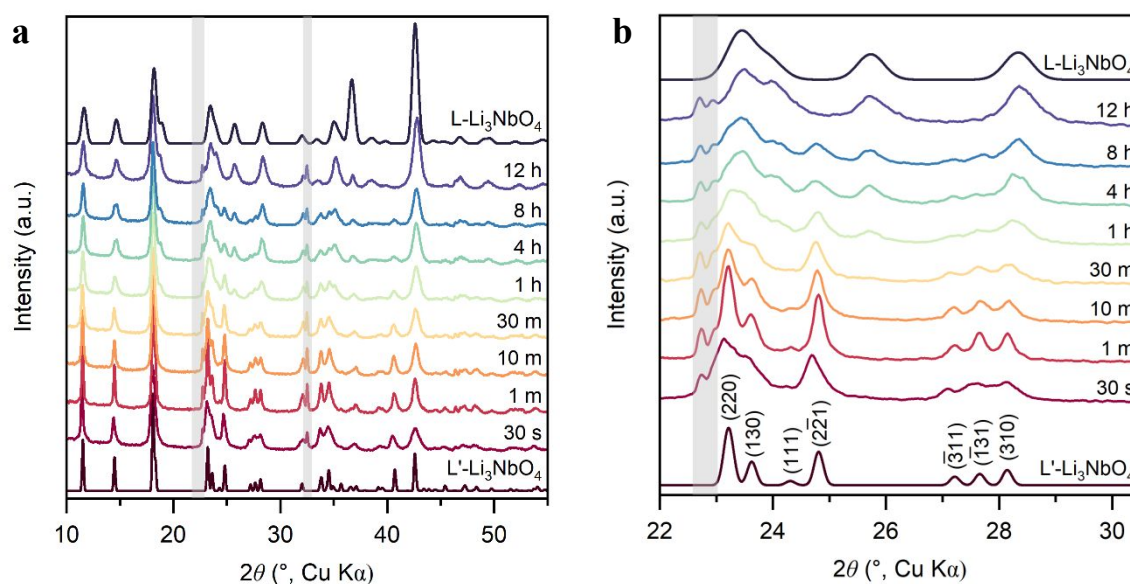
5b, Table 3). The  $^{93}\text{Nb}$  signal from  $\text{NaNbO}_3$  is not obvious in  $\text{L-Li}_3\text{NbO}_4$  as it is only a minor component (2–3%) and its centerband overlaps with a feature of the Nb1 site of  $\text{L-Li}_3\text{NbO}_4$  (Supplementary Figure S2). The  $^{93}\text{Nb}$  spectrum of  $\text{L-Li}_3\text{NbO}_4$  differs from that of  $\text{c-Li}_3\text{NbO}_4$  (Supplementary Figure S7, Table 3) in that the former exhibits two sites while the latter has only one crystallographically unique niobium position. The utility of the quadrupolar coupling parameters becomes apparent here.  $C_Q$  and  $\eta_Q$  of the octahedral  $^{93}\text{Nb}$  site in  $\text{c-Li}_3\text{NbO}_4$  are statistically identical to those of the octahedral Nb2 site of  $\text{L-Li}_3\text{NbO}_4$ ; both of these sites experience  $C_3$  off-centering distortions toward an octahedral face.<sup>47</sup> Contrast this with the octahedral Nb1 site of  $\text{L-Li}_3\text{NbO}_4$  that experiences a  $C_2$  off-centering distortion toward the O2 atoms and has a significantly different quadrupolar NMR lineshape (Figure 1, Figure 5b, Supplementary Figure S7, Table 3). In both  $\text{c-Li}_3\text{NbO}_4$  and  $\text{L-Li}_3\text{NbO}_4$ , these distortions maximize Nb–Nb interatomic distances within the clusters.

$^6\text{Li}$  and  $^7\text{Li}$  NMR were also measured after the ion exchange reaction. The  $^7\text{Li}$  spectrum shows a single isotropic resonance at 0.1 ppm, which is substantially broadened by homonuclear dipolar coupling that is not effectively removed by magic-angle spinning in this lithium-rich compound (Figure 6a). However, the spinning sideband manifold of  $^7\text{Li}$  arising from quadrupolar-broadened  $\pm 3/2$  to  $\pm 1/2$  satellite transitions provides a useful dataset to compare against the calculated nuclear quadrupolar coupling constants for  $\text{L-Li}_3\text{NbO}_4$ , which range from 20 to 100 kHz (Figure 6b, Table 4). A simulation of the  $^7\text{Li}$  spinning sideband manifold at 10 kHz MAS rate with the parameters for  $\text{L-Li}_3\text{NbO}_4$  from Table 4 slightly underestimates the experimental manifold but is a reasonable fit (Figure 6b), particularly considering the high strain indicated by the diffraction data. The  $^6\text{Li}$  NMR spectrum presents a much higher resolution lineshape (Figure 6a). As a nucleus,  $^6\text{Li}$  has a natural abundance of 7.6% and a gyromagnetic ratio that is 38% of  $^7\text{Li}$ . As a result of these nuclear properties,  $^6\text{Li}$  features NMR spectra with minimal residual dipolar broadening. Based on the crystal structure and CASTEP NMR calculations,  $\text{L-Li}_3\text{NbO}_4$  is expected to have six lithium sites with a chemical shift range of 2.2 ppm. Experimentally, three environments were resolved with chemical shifts of 1.33 ppm, 0.14 ppm,  $-0.46$  ppm and a range of 1.79 ppm. Three of the sites have calculated shieldings within 0.07 ppm and appear at the center of the range, which is consistent with the experimental lineshape. Lithium NMR of  $\text{L-Li}_3\text{NbO}_4$  can be compared to that of  $\text{c-Li}_3\text{NbO}_4$  shown in Figure 7.  $^6\text{Li}$  and  $^7\text{Li}$  NMR spectra of  $\text{c-Li}_3\text{NbO}_4$  each feature a single symmetric lineshape centered at  $-0.1$  ppm (Figure 7a). The  $^7\text{Li}$  spinning sideband

manifold can be well simulated with a  $C_Q$  of 35 kHz as indicated by the CASTEP DFT calculations (Figure 7b).



**Figure 7.** (a)  $^{6,7}\text{Li}$  centerband spectra and (b)  $^7\text{Li}$  spinning sideband manifold of  $\text{c-Li}_3\text{NbO}_4$  at 9.4 T and 12.5 kHz MAS. Spectra in (a) are intensity normalized. Centerband truncated in (b). Sideband simulation performed with the calculated  $^7\text{Li}$   $C_Q$  and  $\eta_Q$  parameters for  $\text{c-Li}_3\text{NbO}_4$ .



**Figure 8.** (a) X-ray diffraction patterns of  $\text{L-Li}_3\text{NbO}_4$  as a function of ion exchange time in molten  $\text{LiNO}_3$ . (b) Diffraction pattern region from 22–30.5°  $2\theta$  highlighting the time evolution of peak positions and lineshapes. The shaded region in each figure denotes the position of  $\text{NaNbO}_3$  impurity reflections. The top and bottom curves in each figure are calculated diffraction patterns; intermediate curves are experimental data. See main text for an explanation of  $\text{L}'\text{-Li}_3\text{NbO}_4$ .

**Table 4.**  $^{6,7}\text{Li}$  NMR of  $\text{Li}_3\text{NbO}_4$ .

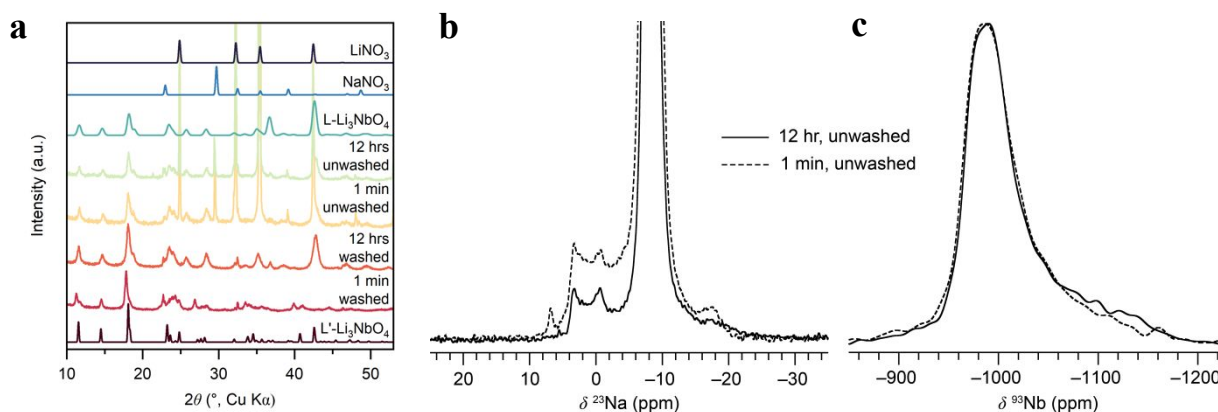
Site	$\sigma_{\text{iso}}$ (ppm)	$\delta_{\text{aniso}}$ (ppm)	$\eta_{\text{CS}}$	$C_Q$ (kHz) <sup>a</sup>	$\eta_Q$
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c-Li <sub>3</sub> NbO <sub>4</sub>	Li1	89.70	−1.36	0.67	−35.2	0.40
	Li1	88.89	−0.57	0.82	20.5	0.55
L-Li <sub>3</sub> NbO <sub>4</sub>	Li2	90.14	−2.09	0.87	−47.5	0.29
	Li3	90.11	−0.35	0.79	55.8	0.99
	Li4	91.07	0.88	0.47	−46.7	0.11
	Li5	90.18	0.72	0.91	55.9	0.10
	Li6	89.59	−3.47	0.47	−99.0	0.69

<sup>a</sup>C<sub>Q</sub> for <sup>7</sup>Li nucleus. <sup>6</sup>Li C<sub>Q</sub>s are scaled by  $Q(^6\text{Li})/Q(^7\text{Li}) = 0.808/40.1$ .<sup>48</sup>

**Ion exchange timescale and mechanism.** In order to better understand the ion exchange process from L-Na<sub>3</sub>NbO<sub>4</sub> to L-Li<sub>3</sub>NbO<sub>4</sub>, a series of time-resolved experiments were carried out by quenching the ion-exchange reaction after 30 s to 12 h. At each time point, XRD, <sup>6</sup>Li, <sup>7</sup>Li, <sup>23</sup>Na, and <sup>93</sup>Nb NMR were measured. Unexpectedly, it was immediately apparent from the diffraction patterns that L-Li<sub>3</sub>NbO<sub>4</sub> formed after a matter of seconds and no residual L-Na<sub>3</sub>NbO<sub>4</sub> peaks were detected (Figure 8).

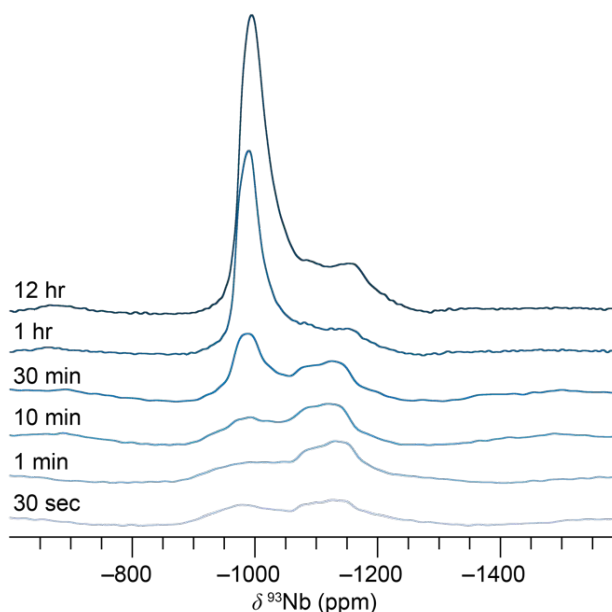
Before discussing this data further, an important caveat is that Na<sub>3</sub>NbO<sub>4</sub> is not stable in water and decomposes to an unknown phase suspected to be a hydrate with its two strongest diffraction peaks at *d*-spacings of 7–8 Å (Supplementary Figure S8). To consider the role of water-washing on the products, diffraction and NMR data were also collected on an unwashed sample after 1 min of ion exchange (Figure 9). There is a large background signal from the (Li,Na)NO<sub>3</sub> flux but the characteristic diffraction peaks of L-Li<sub>3</sub>NbO<sub>4</sub> are apparent while no L-Na<sub>3</sub>NbO<sub>4</sub> (detection limit ~ 2%) nor any other phases are observed (Figure 9a). <sup>23</sup>Na and <sup>93</sup>Nb NMR of the unwashed ion-exchanged sample offer an additional level of detail. The <sup>23</sup>Na NMR spectrum of the unwashed sample exhibits a sharp, high-intensity signal from NaNO<sub>3</sub> at −8.0 ppm and then broader intensity from 10 to −20 ppm (Figure 9b). This latter <sup>23</sup>Na signal decreases with ion-exchange time. The <sup>93</sup>Nb NMR lineshapes of unwashed samples after 1 min or 12 h of ion exchange do not show noticeable differences (Figure 9c). NMR calculations of L-Na<sub>x</sub>Li<sub>3−x</sub>NbO<sub>4</sub> yielded <sup>23</sup>Na and <sup>93</sup>Nb NMR parameters consistent with the experimental spectra (Figure 9b,c, Supplementary Table S4).



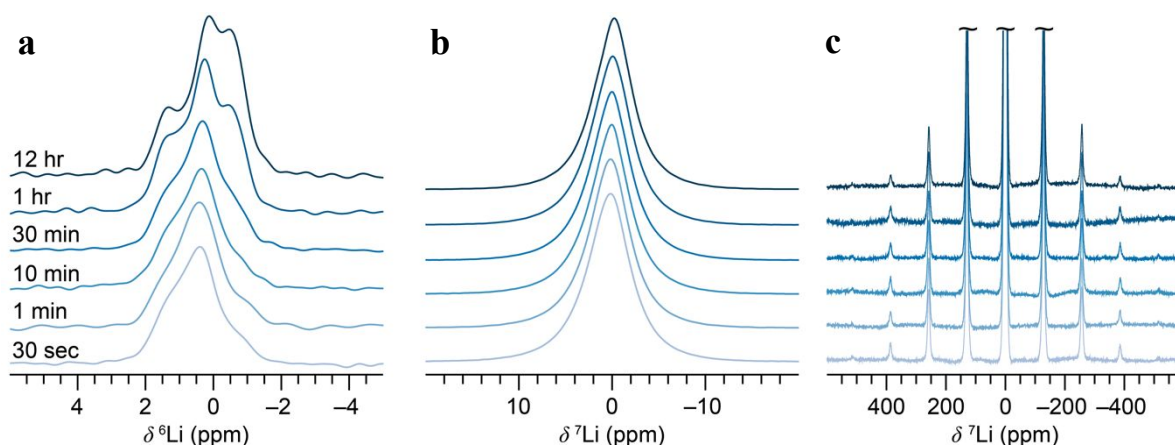
**Figure 9.** (a) XRD, (b)  $^{23}\text{Na}$  and (c)  $^{93}\text{Nb}$  NMR of unwashed  $\text{L-Li}_3\text{NbO}_4$  after 1 min and 12 h of ion exchange.  $^{23}\text{Na}$  and  $^{93}\text{Nb}$  NMR measured at 10 and 39 kHz MAS, respectively, and 9.4 T. Spectra are normalized with respect to sample mass and number of scans. The unwashed sample contains a large quantity of  $\text{LiNO}_3$  and also  $\text{NaNO}_3$  that forms from ion exchange in the flux.

Combining the evidence that (i) residual sodium is present in  $\text{L-Li}_3\text{NbO}_4$ , especially at short reaction times, (ii) that no sodium (other than precursor  $\text{NaNbO}_3$ ) is observed in the  $^{23}\text{Na}$  NMR spectra of the ion-exchange samples after water washing, and (iii) that  $\text{Na}_3\text{NbO}_4$  is unstable in water, it stands to reason that protons replace the residual sodium in  $\text{L-Na}_x\text{Li}_{3-x}\text{NbO}_4$  during the washing process to yield  $\text{L-H}_x\text{Li}_{3-x}\text{NbO}_4$ . Geometry-optimized DFT structures of all  $\text{L-H}_x\text{Li}_{3-x}\text{NbO}_4$  feature hydrogen bonds bridging across two  $[\text{Nb}_4\text{O}_{16}]^{12-}$  clusters. DFT NMR calculations of proton-containing  $\text{L-H}_x\text{Li}_{3-x}\text{NbO}_4$  tended toward large  $^{93}\text{Nb}$  NMR quadrupolar coupling constants (up to  $> 100$  MHz), consistent with the observation that most of the  $^{93}\text{Nb}$  signal is “missing” at short timescales (Figure 10, Supplementary Table S5), which is expected of any  $^{93}\text{Nb}$  site with  $C_Q$  above  $\sim 50$  MHz at 9.4 T.

With this understanding of the secondary ion exchange during the water washing step to remove the flux, we can again consider the time-resolved evolution. Subtle average structure evolution occurs in the diffraction data as a function of ion-exchange reaction times (Figure 8). At short reaction times, XRD from the unwashed and washed samples differ (Figure 8, Figure 9a). However, after 12 h reaction, XRD of washed and unwashed samples are the same, and also match that of the unwashed 1 min phase, which are all consistent with the L- $\text{Li}_3\text{NbO}_4$  lattice parameters derived from



**Figure 10.**  $^{93}\text{Nb}$  NMR of water-washed L- $\text{Li}_3\text{NbO}_4$  as a function of ion exchange time at 39 kHz MAS and 9.4 T. Spectra are normalized with respect to sample mass and number of scans.



**Figure 11.** (a)  $^7\text{Li}$  centerband, (b)  $^7\text{Li}$  sideband manifold, and (c)  $^6\text{Li}$  centerband evolution of L- $\text{Li}_3\text{NbO}_4$  over the course of the ion exchange reaction. Centerband truncated in (c). Spectra are normalized with respect to sample mass and number of scans.

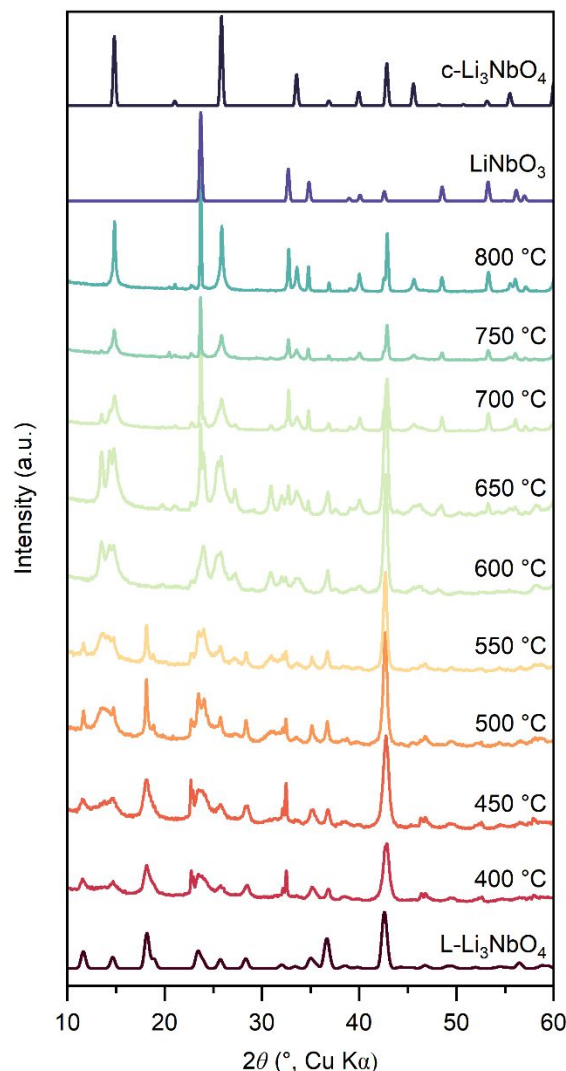
neutron diffraction data (Table 1). The outlier is the washed sample after short ion-exchange time, which can be refined in the same space group as L- $\text{Li}_3\text{NbO}_4$  but with new lattice parameters ( $a = 10.674(1) \text{ \AA}$ ,  $b = 12.225(2) \text{ \AA}$ ,  $c = 5.314(4) \text{ \AA}$ ,  $\beta = 112.689(2)^\circ$ , vol. =  $639.7(2) \text{ \AA}^3$ ); this phase is denoted L'- $\text{Li}_3\text{NbO}_4$ . The L' phase has a 5.4% larger volume and  $3.2^\circ$  larger  $\beta$  angle than the L phase. Taken together, the  $^{23}\text{Na}$  NMR and diffraction data suggest that a small fraction of Na remains after short ion exchange. However, as sodium is ion exchanged for protons during the washing step, the structure relaxes substantially to form the L' phase. High-resolution  $^6\text{Li}$  NMR of the washed samples reveals that there is some redistribution of

the population of intensity within the same 2 ppm region as a function of ion exchange time, likely related to the lattice and proton compositional evolution (Figure 11a). No changes are observed in the  $^7\text{Li}$  centerband or spinning sidebands (Figure 11b,c) and any intensity changes are minor.

Another observation from the ion exchange timescale measurements is that the diffraction peaks are generally sharper at short reaction times (Figure 8a, most easily seen at low  $2\theta$ , e.g.,  $10\text{--}15^\circ$ , where there is no peak overlap). This is in contrast to a typical synthesis where crystallinity increases over time. As will be demonstrated in detail in the next section, L- $\text{Li}_3\text{NbO}_4$  is a metastable compound and the increase in diffraction line broadening over time indicates increasing strain as the structure tries to convert to the ground-state c- $\text{Li}_3\text{NbO}_4$  polymorph.

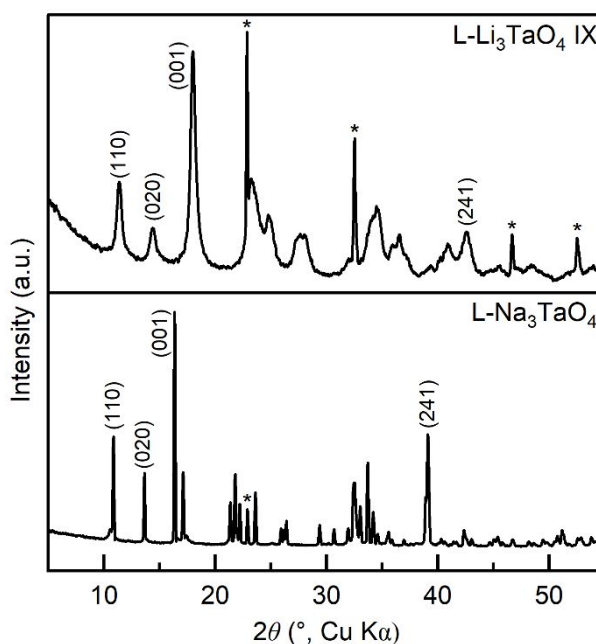
**Variable temperature XRD.** The known high-temperature phase of  $\text{Li}_3\text{NbO}_4$  is cubic with space group  $\bar{I}43m$ .<sup>13,49,50</sup> DFT enthalpy calculations return that c- $\text{Li}_3\text{NbO}_4$  is 6.6 meV per atom more stable than L- $\text{Li}_3\text{NbO}_4$ , a relatively small difference. In order to probe the stability of L- $\text{Li}_3\text{NbO}_4$ , samples were heated from 400 to 800 °C for 12 h (Figure 12; n.b., nine different samples heated individually to 400 °C, 450 °C, etc., not one sample ramped up in temperature). Between 550–600 °C, L- $\text{Li}_3\text{NbO}_4$  peaks disappeared. Slightly earlier, at 500 °C, an unidentified intermediate started to form with broad intensity at 13.5 and 30.9°  $2\theta$ , those reflections narrowed at temperatures up to 650 °C and then disappeared by 750 °C. At 650 °C, reflections from  $\text{LiNbO}_3$  appeared, owing to the understoichiometry of lithium in the samples that is consistent with the aforementioned discussion of proton exchange for residual sodium according to:  $\text{H}_x\text{Li}_{3-x}\text{NbO}_4 \rightarrow (1-x/2)\text{Li}_3\text{NbO}_4 + x/2\text{LiNbO}_3 + x/2\text{H}_2\text{O}$  upon heating.

Although there is not a group–subgroup relationship between  $\bar{I}43m$  and  $C2/m$ , some of the reflections from c- $\text{Li}_3\text{NbO}_4$  and L- $\text{Li}_3\text{NbO}_4$  are in very similar positions owing to the similarity of their unit cells which both have  $Z = 8$  and volumes of 598.6 Å<sup>3</sup> and 606.7 Å<sup>3</sup>, respectively.



**Figure 12.** Phase transition of L- $\text{Li}_3\text{NbO}_4$  to c- $\text{Li}_3\text{NbO}_4$  as a function of temperature.

**Extension to L-Na<sub>3</sub>TaO<sub>4</sub>.** Based on the results for L-Li<sub>3</sub>NbO<sub>4</sub>, an obvious question was whether this methodology could be extended to the tantalum system. The ground state phase L-Na<sub>3</sub>TaO<sub>4</sub> is isostructural with L-Na<sub>3</sub>NbO<sub>4</sub>, while the known lithium-rich tantalates have unique crystal chemistry. Li<sub>3</sub>TaO<sub>4</sub> has at least two known polymorphs,  $\alpha$  and  $\beta$ , which both comprise kinked chains of edge-sharing TaO<sub>6</sub> octahedra.<sup>18,20</sup> Ion exchange of L-Na<sub>3</sub>TaO<sub>4</sub> in molten lithium nitrate yielded L-Li<sub>3</sub>TaO<sub>4</sub> (Figure 13, Table 5). The DFT calculated enthalpy of L-Li<sub>3</sub>TaO<sub>4</sub> is 6.8 meV per atom higher than the solid-state synthesized phase  $\beta$ -Li<sub>3</sub>TaO<sub>4</sub>. The lattice parameters of the ion exchanged phase suggest that some Na<sup>+</sup> was left in the structure even after 12 h ion exchange, which was subsequently exchanged for H<sup>+</sup> (Table 5, Supplementary Table 3).

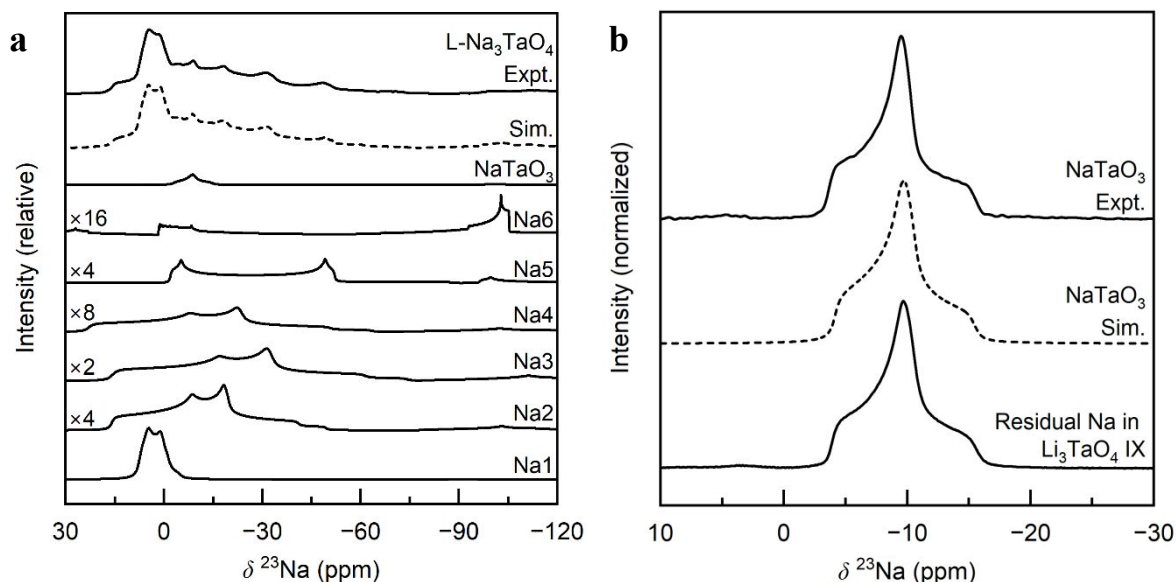


**Figure 13.** X-ray diffraction patterns of L-Na<sub>3</sub>TaO<sub>4</sub> and L-Li<sub>3</sub>TaO<sub>4</sub> after 12 h of ion exchange in a molten lithium salt. Some of the most prominent reflections are labeled. Asterisks denote observed NaTaO<sub>3</sub> reflections.

**Table 5.** Lattice parameters of L-Na<sub>3</sub>TaO<sub>4</sub> and L-Li<sub>3</sub>TaO<sub>4</sub> from refinement of the structures with laboratory X-ray powder diffraction data.

Layered C2/m	L-Na <sub>3</sub> TaO <sub>4</sub>	L-Li <sub>3</sub> TaO <sub>4</sub>	$\Delta$ (%)
$a$ (Å)	11.145(3)	10.63(2)	−4.6
$b$ (Å)	13.0044(5)	12.187(4)	−6.3
$c$ (Å)	5.7601(7)	5.316(6)	−7.7
$\beta$ (°)	109.657(3)	112.22(3)	
Volume (Å <sup>3</sup> )	786.21(6)	637.69(3)	−18.9

Experimental  $^{23}\text{Na}$  NMR of  $\text{L-Na}_3\text{TaO}_4$  was in excellent agreement with the spectrum calculated from the structure model (Figure 14a, Table 6). Analogously to the niobium system, a small impurity of  $\text{NaTaO}_3$  was observed after the synthesis of  $\text{L-Na}_3\text{TaO}_4$  and remained present through the ion exchange and washing steps. After lithium ion exchange and water-washing to remove the flux,  $\text{NaTaO}_3$  was the only residual  $^{23}\text{Na}$  resonance (Figure 14b).<sup>51</sup>



**Figure 14.** (a)  $^{23}\text{Na}$  NMR of  $\text{L-Na}_3\text{TaO}_4$ . The simulated  $^{23}\text{Na}$  spectrum in (a) includes contributions from the six unique sodium sites in the crystal structure and the  $\text{NaTaO}_3$  impurity. Broader sites in (a) are scaled up in intensity, as denoted, to better show their lineshapes. (b) Experimental and simulated  $^{23}\text{Na}$  spectrum of  $\text{NaTaO}_3$  compared to the residual  $^{23}\text{Na}$  lineshape observed in  $\text{L-Li}_3\text{TaO}_4$  after ion exchange.

**Table 6.**  $^{23}\text{Na}$  NMR of  $\text{Na}_3\text{TaO}_4$  and  $\text{NaTaO}_3$ .

		<u>calculated</u>					<u>experimental<sup>a</sup></u>		
	Site	$\sigma_{iso}$ (ppm)	$\delta_{aniso}$ (ppm)	$\eta_{CS}$	$C_Q$ (MHz)	$\eta_Q$	$\delta_{iso}$ (ppm)	$C_Q$ (MHz)	$\eta_Q$
L-Na <sub>3</sub> TaO <sub>4</sub>	Na1	554.8	11.5	0.14	1.56	0.36	8.7	1.5(1)	0.36(4)
	Na2	546.5	−20.9	0.81	−3.24	0.66	17.2	3.3(2)	0.70(2)
	Na3	544.1	−15.1	0.28	−3.90	0.67	17.3	3.9(2)	0.67(2)
	Na4	542.6	−13.0	0.60	−3.83	0.66	23.8	3.8(2)	0.66(2)
	Na5	550.4	−11.6	0.33	−4.27	0.06	10.8	4.2(2)	0.06(2)
	Na6	549.0	−27.9	0.57	5.82	0.64	n/r	n/r	n/r
NaTaO <sub>3</sub>	Na1						−3.5	1.35(1)	0.93(3)

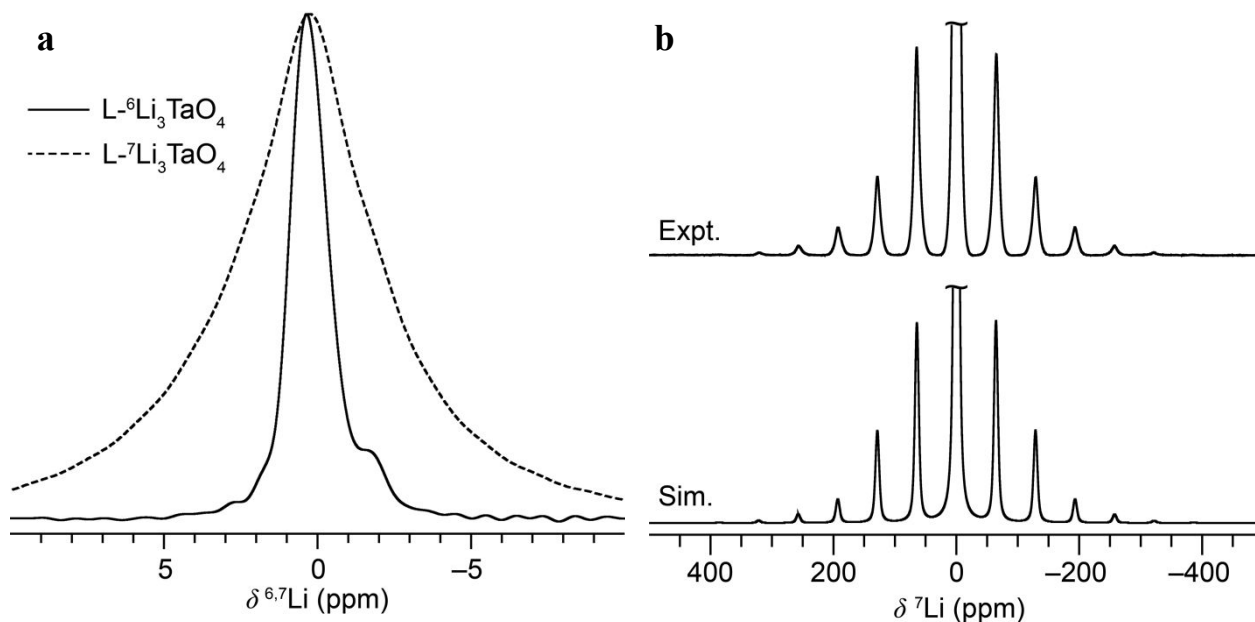
<sup>a</sup>Experimental values obtained by first simulating the GIPAW calculated values and then refining the isotropic chemical shift and the quadrupolar coupling magnitude and asymmetry to obtain a best-fit of the simulation to the experimental data.

$^6\text{Li}$  and  $^7\text{Li}$  spectra of ion exchanged L- $\text{Li}_3\text{TaO}_4$  (Figure 15, Table 7) and solid-state synthesized  $\beta\text{-Li}_3\text{TaO}_4$  (Figure 16, Table 7) show distinction only between the  $^6\text{Li}$  centerbands. This is consistent with the calculated lithium NMR parameters suggesting a 0.1 ppm chemical shift range for the three lithium sites in  $\beta\text{-Li}_3\text{TaO}_4$  and a 1.4 ppm chemical shift range for the six lithium sites in L- $\text{Li}_3\text{TaO}_4$ ; whereas both have  $^7\text{Li}$   $C_Q$ s ranging from 21–104 kHz.

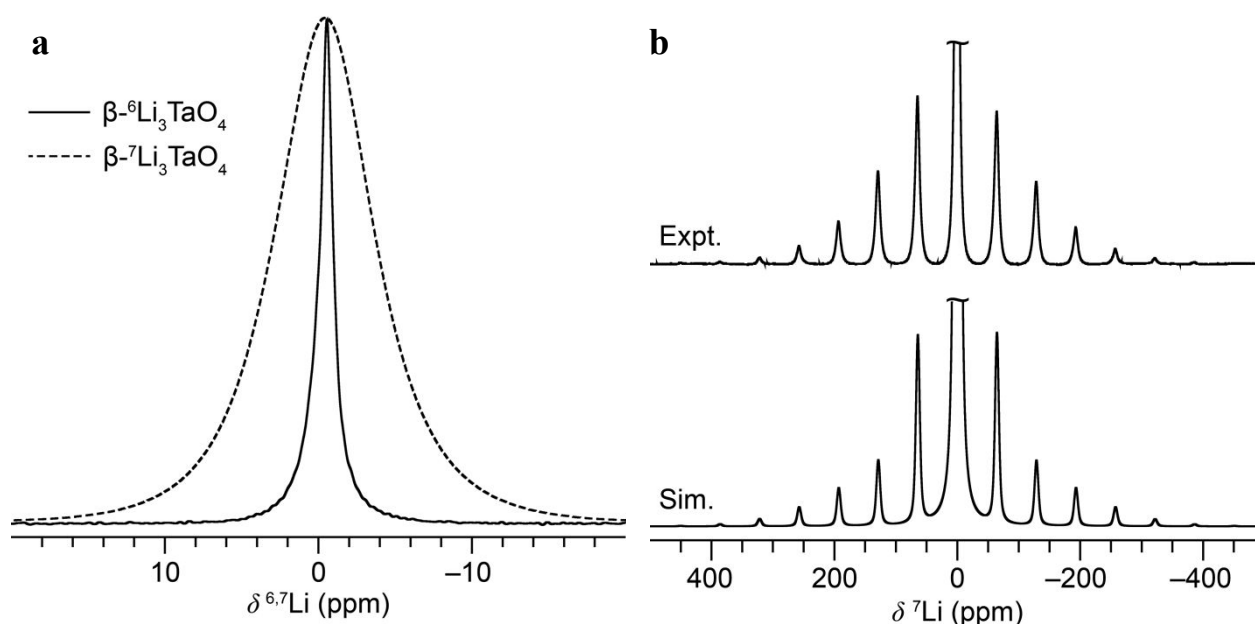
**Table 7.**  $^6,^7\text{Li}$  NMR of  $\text{Li}_3\text{TaO}_4$ .

	Site	$\sigma_{iso}$ (ppm)	$\delta_{aniso}$ (ppm)	$\eta_{CS}$	$C_Q$ (kHz) <sup>a</sup>	$\eta_Q$
$\beta\text{-Li}_3\text{TaO}_4$	Li1	91.01	1.51	0.8	−20.9	0.97
	Li2	90.92	−1.11	0.59	103.7	0.71
	Li3	90.99	1.38	0.56	25.1	0.64
L- $\text{Li}_3\text{TaO}_4$	Li1	90.15	−0.84	0.47	20.8	0.71
	Li2	91.06	3.11	0.97	48.9	0.92
	Li3	90.88	1.22	0.53	62.1	0.52
	Li4	91.55	2.08	0.91	−65.7	0.01
	Li5	90.99	1.24	0.39	52.6	0.28
	Li6	90.66	3.18	0.32	−104.3	0.58

<sup>a</sup> $C_Q$  for  $^7\text{Li}$  nucleus.  $^6\text{Li}$   $C_Q$ s are scaled by  $Q(^6\text{Li})/Q(^7\text{Li}) = 0.808/40.1$ .<sup>48</sup>



**Figure 15.** (a)  $^6,^7\text{Li}$  centerband spectra and (b)  $^7\text{Li}$  spinning sideband manifold of L- $\text{Li}_3\text{TaO}_4$  at 9.4 T and 10 kHz MAS. Spectra in (a) are intensity normalized. Centerband truncated in (b). Sideband simulation performed with the calculated  $^7\text{Li}$   $C_Q$  and  $\eta_Q$  parameters for L- $\text{Li}_3\text{TaO}_4$ .



**Figure 16.** (a)  $^{6,7}\text{Li}$  centerband spectra and (b)  $^7\text{Li}$  spinning sideband manifold of  $\beta\text{-Li}_3\text{TaO}_4$  at 9.4 T and 10 kHz MAS. Spectra in (a) are intensity normalized. Centerband truncated in (b). Sideband simulation performed with the calculated  $^7\text{Li}$   $C_Q$  and  $\eta_Q$  parameters for  $\beta\text{-Li}_3\text{TaO}_4$ .

Owing to the instability of  $\text{Na}_3\text{NbO}_4$  and  $\text{Na}_3\text{TaO}_4$  in water, conventional ambient temperature aqueous ion exchange reactions in these systems are not possible. However, preliminary tests indicate that non-aqueous ion exchange at 22 °C is possible, which is a future direction to explore proton-free lithium-rich niobates and tantalates. Given their layered structures, it would also be interesting to explore the  $\text{Li}^+$  conductivity of these phases, which, together with electrochemical stability studies, would help establish the relevance of these new materials as solid electrolytes in solid-state batteries.

## Conclusions

Two new lithium-rich early transition metal oxides with layered structures and non-close-packed oxygen atoms— $\text{L-Li}_3\text{NbO}_4$  and  $\text{L-Li}_3\text{TaO}_4$ —have been synthesized via molten salt ion exchange chemistry. Topotactic exchange occurred despite that the volume change is ca. 20% and that the basic building units of layered  $\text{Na}_3\text{MO}_4$  ( $M = \text{Nb}, \text{Ta}$ ) are 0D clusters. X-ray and neutron diffraction,  $^{6,7}\text{Li}$ ,  $^{23}\text{Na}$ , and  $^{93}\text{Nb}$  solid-state NMR, and DFT calculations were combined to provide a detailed look at the crystal chemistry and transformation process. Time-stepped measurements revealed that some  $\text{Na}^+$  remains, which gets replaced by  $\text{H}^+$  during the washing process that removes the salt flux. As a function of ion exchange time,  $^{93}\text{Nb}$  NMR lineshapes sharpen while diffraction reflections broaden. This difference in the local and long-range structure evolution can be attributed to the different broadening mechanisms:  $^{93}\text{Nb}$   $C_Q$ s increase when  $\text{H}^+$  is present ( $\text{H}^+$  decreases with time) while XRD peaks broaden because the

structure is metastable and wants to transform to c-Li<sub>3</sub>NbO<sub>4</sub> (strain increases with time). Coplanar octahedra in the [Nb<sub>4</sub>O<sub>16</sub>]<sup>12-</sup> cluster in L-Li<sub>3</sub>NbO<sub>4</sub> transform into the supertetrahedral arrangement in c-Li<sub>3</sub>NbO<sub>4</sub> above 550 °C. Residual protons in L-Li<sub>3</sub>NbO<sub>4</sub> represent a lithium deficiency that lead to the formation of LiNbO<sub>3</sub> upon heating. Soft-chemical synthesis together with NMR crystallography is a powerful combination for the realization and detailed understanding of new metastable materials in compositional phase spaces such as lithium-rich metal oxides that have proven difficult to access and characterize owing to the large quantity of light alkali elements and/or the presence and role of protons. A more general takeaway is that topotactic ion exchange of non-framework structures, even with extremely large volume changes, is not only possible but can be a rapid route to produce new compounds.

### **Associated Content**

*T*<sub>1</sub> relaxation data, NMR measurement details, additional diffraction and NMR data, scanning electron microscopy images, particle size distributions, calculated parameters of mixed H/Li/Na phases.

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### **Notes**

The authors declare no competing financial interest.

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