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In situ Neutron Diffraction Studies of Ion Exchange Synthesis Mechanism of $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$: Evidence for Hidden Phase Transition

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ABSTRACT: Motivated by predictions made using a bond valence sum difference map (BVS-DM) analysis, the novel Li-ion conductor $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ was synthesized by ion exchange from a $\text{Na}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ precursor. Impedance spectroscopy measurements indicate that $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ has a room temperature Li-ion conductivity of about 10^{-6} S/cm (comparable to LiPON) which is six orders of magnitude higher than the extrapolated Na-ion conductivity of $\text{Na}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ at this temperature. The structure of $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ was determined from *ex situ* synchrotron and time-of-flight neutron diffraction data to retain the $P2_13$ space group, though with a cubic lattice parameter of $a = 9.11176(8)$ Å that is significantly smaller than the $a = 9.2439(1)$ Å of $\text{Na}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$. The two Li-ion sites are found to be very substantially displaced (~ 0.5 Å) relative to the analogous Na sites in the precursor phase. The non-molten salt ion exchange method used to prepare $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ produces a minimal background in powder diffraction experiments, and was therefore exploited to for the first time follow a Li^+/Na^+ ion exchange reaction using *in situ* powder neutron diffraction. Lattice parameter changes during ion exchange suggest that the reaction proceeds through a $\text{Na}_{2-x}\text{Li}_x\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ solid solution (Stage 1) followed by a two-phase reaction (Stage 2) to form $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$. However, full Rietveld refinements of the *in situ* neutron diffraction data indicate that the actual transformation mechanism is more complex and instead involves two thermodynamically distinct solid solutions in which the Li exclusively occupies the Li1 site at low Li contents (Stage 1a) and then migrates to the Li3 site at higher Li contents (Stage 1b), a crossover driven by the different signs of the local volume change at these sites. In addition to highlighting the importance of obtaining full structural data *in situ* throughout the ion exchange process, these results provide insights into the general question of what constitutes a thermodynamic phase.

1. Introduction

It has been known for many years that low valence cations can exhibit significant mobility within solid state inorganic compounds, even at room temperature. Some of the initial systems in which room temperature ionic conductivity were observed include clays and zeolitic inorganic framework compounds.¹⁻² These compounds were initially investigated for chemical applications associated with inorganic ion exchange, with targeted applications including nuclear waste remediation, water softening, chromatographic separation and catalysis.³⁻⁶ More recently, the mobility of ions in solids has been investigated for energy technology applications including rechargeable batteries⁷⁻⁹ and fuel cells.¹⁰⁻¹¹ systems in which the mobility of both electrons and ions must be managed.

For Li-ion batteries, solid state electrolytes can have a number of substantial advantages over liquid electrolytes.¹²⁻¹⁴ The first is stability over wider range of voltages, which can increase the overall energy density of a battery device. While the operating voltages of most Li-ion batteries are generally less than 4 V due to side reactions that can occur at very high or very low voltages, solid state electrolytes may enable cathodes to operate at higher voltages and thus allow more energy to be contained within each stored electron. Second, there are many undesirable degradation pathways of liquid electrolytes, and the use of a solid state electrolyte may substantially inhibit chemical degradation, thus improving the lifetime of batteries. Solid state electrolytes should also improve the safety of Li-ion batteries by both eliminating the flammable organic sol-

vents and the toxic and hazardous soluble electrolyte salts such as LiPF_6 or LiClO_4 commonly used with these solvents. Finally, a solid state electrolyte may enable the use of Li metal anode, which can deliver a very high energy density and thus greatly increase the full cell battery energy. However, these many advantages for battery applications have been offset by the challenges of finding solid state electrolytes with good ionic conductivities at or near room temperature. The development of novel solid state electrolytes with improved ionic conduction may thus have a transformative impact on energy storage technologies.

The elucidation of design principles for the next generation of solid state electrolytes requires accurate structural data, which is need to gain meaningful insights into the likely diffusion paths and activation energies for ion motion.^{8-9, 15} A powerful technique for obtaining structural information for polycrystalline solid state compounds is powder neutron diffraction, whose advantages over conventional X-ray diffraction techniques typically include better sensitivity to light atoms, form factors which decay more slowly (allowing diffraction peaks intensities to be more effectively measured), and a highly-penetrating beam which often allows the totality of bulk samples to be simultaneously probed in a manner that is very useful for *in situ* experiments.¹⁶⁻²³ Despite these clear advantages, the technique of powder neutron diffraction has not previously been applied to study Li^+/Na^+ ion exchange processes *in situ*, likely due to the challenges of working with liquids (either organic electrolytes or molten salts) in powder

diffraction experiments. Ion exchange reactions are traditionally carried out using either molten salts (e.g., a LiCl/LiNO₃ eutectic mixture)²⁴ or highly concentrated Li⁺ solutions (e.g., LiBr in acetonitrile or hexanol)²⁵. These liquids produce a strong and diffuse background in diffraction experiments that is difficult to model and severely increases the noise in the measurement of Bragg peak intensities. Furthermore, molten salts are highly reactive and attack standard containers for *in situ* experiments (glass capillaries, vanadium cans, etc.), while the large amount of hydrogen in liquid organic solvents makes them inappropriate for neutron diffraction studies due to the large incoherent background produced by this element.

We have recently discovered that the ion exchange of Li ions into Na-containing precursors can be effectively accomplished using a solid, non-molten Li salt instead of the liquid ion sources which have been exclusively used in the prior battery literature.²⁶⁻²⁸ Intriguingly, the use of a non-molten Li salt offers tremendous advantages for *in situ* diffraction experiments since the reactivity with the container walls is negated, and the scattering from the Li salt is concentrated in a few sharp Bragg peaks rather than dispersed in a diffuse background. Here, it is demonstrated that *in situ* neutron diffraction can be used to follow fine details of the evolution in structure and bonding throughout the ion exchange synthesis used to prepare the novel compound Li₂Mg₂P₃O₉N, a new Li-ion conductor that could not be directly synthesized from stoichiometric precursors and could instead only be prepared through ion exchange of an isostructural precursor, Na₂Mg₂P₃O₉N. This represents the first-ever use of *in situ* neutron diffraction to study a Li⁺/Na⁺ ion exchange reaction, and the *in situ* neutron methods demonstrated here can be generally applied to accelerate the discovery and optimization of metastable compounds produced by ion exchange. The synthesis mechanism of Li₂Mg₂P₃O₉N revealed from neutron diffraction was found to involve an unexpected extra phase transition within the solid solution regime whose origin provide insights into the general question of what constitutes a thermodynamic phase.

2. Experimental

Na₂Mg₂P₃O₉N was synthesized by using a method similar to the original preparation route for this phase²⁹. Stoichiometric amounts of NaPO₃ (Fisher Scientific, n ~ 6), MgO (Alfa Aesar, 99.9%) and (NH₄)₂HPO₄ (AMRESCO, >99%) were mixed together, hand ground, and then milled for 90 min in an agate vibratory ball mill (Fritsch Pulverisette 0) with a 120 mm diameter ball. The mixture was then placed on a boat constructed from Mo foil (99.985%, Alfa Aesar, 0.025 mm thick), which was loaded into a 1 inch diameter quartz tube inside a horizontal tube furnace (Minimite, Lindberg/BlueM). The tube was purged with a high flow rate of NH₃ gas, and then switched to a lower flow rate of 50 mL/min for the synthesis reaction. The sample was heated directly to 780 °C (ramp rate of 200 °C/h), held for 20 hours, and cooled down to room temperature inside the furnace. The white as-prepared Na₂Mg₂P₃O₉N powder was then ground and stored in a desiccator for characterization experiments.

In order to prepare Li₂Mg₂P₃O₉N *ex situ*, about 0.65 g Na₂Mg₂P₃O₉N were combined with anhydrous LiBr (SPECTRUM, >99%) in a molar ratio of 1:10 (Na to Li) in an argon-filled glove box. The mixture was ground in an agate

mortar and pestle, placed in a 50 mL Al₂O₃ crucible, and stored in a desiccator prior to reaction. For the ion exchange reaction, the powder mixture was loaded into a 3" diameter mullite tube inside a horizontal tube furnace (SV series, Melten), which was then purged with N₂ gas. Ion exchange was carried out at 330 °C for 20 hours under flowing N₂. The reaction product was washed with methanol 5 times, washed twice with acetone, and was finally dried in an oven at 120 °C. After the fourth repetition of the ion-exchange process, no further peak shift was seen in X-ray diffraction patterns. About 0.4 g Li₂Mg₂P₃O₉N could be recovered at the end of the non-molten ion exchange process (~60% yield).

For *in situ* neutron diffraction studies, ⁷LiCl powder was used as the lithium source to eliminate the strong absorption that occurs when natural Li is used. To synthesize dehydrated ⁷LiCl, about 5 grams ⁷Li₂CO₃ (Sigma Aldrich, >99% atom) was dissolved into 500 ml of a ~0.5 M HCl solution, (1:4 molar ratio of ⁷Li₂CO₃ to HCl). The mixture was stirred using a magnetic stir bar for about 30 min until a transparent solution was formed, and then was heated to 150 °C to evaporate residual water and excess HCl. The white powder of hydrated ⁷LiCl was collected and transferred to a 50 ml alumina crucible and further dried at 400 °C for 12 hours, and immediately transferred while hot into a home-made desiccator and then into an argon filled glove box in which the sample was fully cooled down to room temperature. For neutron experiments, 1.5 g of the as-prepared Na₂Mg₂P₃O₉N powder was ground together with 1.5 grams of ⁷LiCl in a glove box using an agate mortar and pestle (Li:Na molar ratio of ~4:1), then placed in a closed glass vial and heat sealed in a plastic bag for shipping. At the neutron source, the sample was transferred into a 6 mm thin walled vanadium can inside a helium-filled glove box, which was then attached to the end of the cryofurnace sample stick. No corrosion of the V can during ion exchange was observed.

Laboratory X-ray diffraction (XRD) data were collected on a Bruker D8 Advance diffractometer utilizing Cu K_α radiation from a long fine focus X-ray tube (K_{α1} = 1.54053 Å, K_{α2} = 1.54431 Å). The system was operated at a 300 mm working radius with a 1D position-sensitive LynxEye Si detector with 192 channels. An approximate step size of 0.02° and a count time of 1 s/step were used for routine continuous scans. Synchrotron XRD data were collected at the X 14A beam line of the National Synchrotron Light Source at Brookhaven National Laboratory. Data were collected using a 1D linear position sensitive silicon strip detector with 640 channels at a distance of 1433 mm, and the final patterns for refinement was obtained by merging data sets collected at a number of different fixed angles.

Time-of-flight powder neutron diffraction data were collected on the NOMAD and POWGEN powder diffraction beamlines at the Spallation Neutron Source (SNS) of Oak Ridge National Laboratory (ORNL). For room temperature *ex situ* NOMAD experiments, about 150 mg of powder were packed into a 3 mm diameter quartz capillary, an arrangement which minimizes absorption effects. Typical data collection times were 120 – 140 min. The NOMAD data were reduced using custom beamline software³⁰ in a manner that allowed both the analysis of Bragg diffraction data through Rietveld refinement and pair distribution function (PDF) data. For *in situ* experiments on POWGEN, about 1.5 grams of sample

1 were packed into a 6 mm vanadium can, and then loaded into
2 a cryofurnace (JANIS) which was operated under vacuum ($< 10^{-5}$ bar). The temperature of the system was calibrated using
3 diffraction data from a $\text{MgO}/\text{Al}_2\text{O}_3$ standard mixture and the
4 previously determined thermal expansion properties of the
5 standard materials. Neutron diffraction data from POWGEN
6 were reduced using the MANTID software.³¹ In all cases, data
7 were normalized to the scattering of a V rod (after stripping
8 Bragg peaks and smoothing).

9 For the *in situ* ion-exchange experiment, temperature-
10 dependent neutron diffraction data were collected at nine differ-
11 ent temperatures during the initial ramp from 300 K to 605
12 K during the ion exchange process. At each temperature, the
13 sample was equilibrated for 15 min before starting a 60 min
14 data collection. While holding at 605 K for 13 hours, data
15 were continuously collected in consecutive 30 min scans. The
16 furnace was then allowed to cool naturally, and three more
17 scans of 2, 2, and 0.5 h in length were carried out during cool-
18 ing. Finally, a 1 h scan was collected at 300 K at the end of
19 the experiment.

20 Rietveld refinements of crystal structures were carried out
21 using the TOPAS software package (Bruker-AXS, v4.2), with
22 additional refinements carried out in JANA 2006³² to generate
23 Fourier difference maps, which were plotted using VESTA.³³
24 The conversion from time-of-flight to *d*-spacing was done
25 using 2nd degree polynomial parameters refined from a LaB_6
26 standard sample. The peak shapes were primarily modeled
27 using a pseudo-Voigt function, with an additional exponential
28 convolution used to model the extended peak tails on the high
29 *d*-spacing side of the peaks. No absorption correction was
30 applied to the NOMAD data, since the absorption from the
31 sample and the capillary were both very small. For POWGEN
32 data, an estimated linear absorption coefficient of $\mu_L = 0.4$
33 cm^{-1} was used to model the absorption from both the sample
34 and the V can. While this correction is adequate, it does not
35 perfectly account for the merging of data of different wave-
36 lengths to form a single peak, and both the refined absorption
37 coefficient and the refined displacement parameters should be
38 considered approximate. When analyzing the diffraction data
39 from the isothermal 605 K hold, displacement parameters ob-
40 tained at all times were constrained to be equal during this
41 hold. PDF data were fit using the PDFGUI software package³⁴
42 using the average structure obtained from Rietveld refinement
43 as the starting model.

44 Scanning electron microscopy (SEM) images and energy
45 dispersive X-ray (EDX) spectra were collected on a JEOL
46 7600 instrument. Uncoated powders were loaded onto carbon
47 tape for measurements. The data collection and analysis was
48 carried out using the INCA software. The SEM was operated
49 at 5 kV in low vacuum condition during imaging to minimize
50 charging effects. For EDX data collection, the operation volt-
51 age was 15 kV.

52 The ^7Li NMR measurements were performed on an 8.46 T
53 Wide-bore Varian Chemagnetics Infinity Plus 360 MHz spec-
54 trometer equipped with a 1.8 mm HX probe (Argo Samoson).
55 The as-prepared $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ powder was packed into a 1.8
56 mm silicon nitride rotor and spun at 36 kHz. A rotor-
57 synchronized spin echo sequence (π pow₁-pow₂-acquisition)
58 was utilized with a pulse width of 1.85 μs and a recycle delay
59

of 1 s. The ^7Li chemical shift of 0 ppm was externally refer-
enced to 1 M LiCl solution.

Alternating current (ac) impedance spectroscopy was uti-
lized to evaluate lithium ionic conductivity in the as-prepared
 $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$. The well ground $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ powder was
pressed into a 1/4" diameter pellet in an isostatic press generat-
ing a pressure of ~ 1 GPa. The density of this pellet was de-
termined to be 92%. The pellet was further polished and coat-
ed with a thin layer of Pt on each side, and then mounted in a
spring-loaded Teflon cell which was wrapped with aluminum
foil and placed into a steel can. Shielded copper wire was
used to connect the Teflon cell to a coaxial cable interfaced
with an impedance spectrometer, which was a HP 4192A (5
Hz – 13 MHz, peak-to-peak polarization potential of 200 mV)
for the initial room temperature measurement and a Biologic
VMP3 (50 mHz – 1 MHz, 100 mV ac potential) for all subse-
quent measurements.

3. Results and discussion

3.1 Synthesis and ionic conductivity of $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$

Figure 1. $\text{Na}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ (2:2) crystal structure with MgO_6 octa-
hedra shown in brown and PO_3N tetrahedral trimers in green, with
the local environments of Na1 and Na3 shown below. The two
sodium sites are labeled as Na1 and Na3 to be consistent with
nomenclature in $\text{Na}_3\text{AlP}_3\text{O}_9\text{N}$ -type (3:1) compounds.¹⁵

It is known that cubic nitridophosphates can serve as cath-
odes for both Li-ion (e.g. $\text{Li}_2\text{Fe}_2\text{P}_3\text{O}_9\text{N}$)³⁵ and Na-ion batter-
ies (e.g. $\text{Na}_3\text{TiP}_3\text{O}_9\text{N}$)¹⁵ and these compounds have previously
been termed CUBICONs due to the good ion conduction with-
in their cubic lattice. Given the inherent ionic conductivity of
this structure type, the more electronically insulating analo-
gues of these compounds, including $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ and
 $\text{Na}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ could potentially have applications as solid
state electrolytes. Although $\text{Na}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ was reported to be
a poor Na-ion conductor unless heated well above room tem-
perature ($\sigma_i = 1.0 \times 10^{-5}$ S/cm at 440 °C with an activation en-
ergy of $E_a = 0.78$ eV),³⁶ we have previously found that the
mobility of Li-ions within the CUBICON framework can be
much higher than that of Na-ions,³⁵ and thus $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$

was chosen as a target of the present work. However, there are no previous reports of the existence of $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$, and present efforts to synthesize this novel phase at a variety of temperatures using methods analogous to those used to prepare the Na-analogue were unsuccessful, suggesting that this phase is at best a metastable compound which can only be accessed through indirect syntheses such as ion exchange.

$\text{Na}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ is a thermodynamically stable phase which can be directly synthesized in bulk amounts by solid state ammonolysis,^{29, 36} a necessary first step in order to have sufficient sample to explore ion exchange reactions with Li to produce $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$. Laboratory X-ray diffraction patterns of the white $\text{Na}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ powders resulting from ammonolysis reactions showed no evidence of impurity phases, and indicated that the cubic nitridophosphate had good crystallinity. For these single phase samples, high quality structural data was obtained by Rietveld refinement against both synchrotron (X14A, NSLS) and neutron diffraction data (NOMAD, SNS). Refinements confirmed the expected space group of $P2_13$ (#198), with a cubic lattice parameter of $a = 9.2439(1)$ Å refined from the synchrotron data. The details of the method and the refined crystallographic parameters are presented in the Supporting Information (Figure S1 and S2, Tables S1-S4), with the structure obtained from this refinement shown in Figure 1. The $\text{Na}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ neutron data provided high sensitivity to the light atoms (O, N) due to the large nuclear scattering length of these atoms, and supported the refinement of anisotropic displacement parameters for all sites as well as the precise determination of bond lengths.

Figure 2. Comparison of (a) Cu K α XRD patterns and (b) SEM-EDX spectra of pristine $\text{Na}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ and ion-exchanged $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$.

Traditional ion exchange methods could not produce single-phase $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$, as the use of low-melting molten salts (e.g. LiNO_3) was found to result in partial framework decomposition while the use of Li salts in low-boiling organic solvents was ineffective for achieving full Na removal due to the slow nature of the process at low temperatures. Instead, $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ was prepared using low temperature non-molten salt ion-exchange methods which we originally developed to

produce $\text{Li}_{2-x}\text{Fe}_2\text{P}_3\text{O}_9\text{N}$ cathodes³⁵ were applied to replace the Na^+ cations in $\text{Na}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ with Li^+ . Although solid-solid Li-ion exchange reactions are generically expected to be much slower than analogous liquid-solid reactions due to both the reduced surface contact area and the reduced mobility of Li^+ , *ex situ* X-ray diffraction studies clearly indicated that Li^+ ions diffuse sufficiently well to be introduced into $\text{Na}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ at 330 °C using LiBr as the Li^+ source (Figure 2a), a temperature well below its melting point of 550 °C. SEM-EDX spectra confirmed that the removal of Na^+ ions is essentially complete after the fourth exchange cycle (Figure 2b and Figure S3 and S4), resulting in the production of the novel phase $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$. The cubic lattice parameter of $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ ($a = 9.1118$ Å) is substantially reduced relative to that of $\text{Na}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ ($a = 9.2439$ Å).

The structure of the novel phase $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ was determined through combined refinement against synchrotron X-ray and time-of-flight (TOF) neutron powder diffraction data, as reported in Figure 3, Table 1 and Table S5. From this data it is clear that the CUBICON structure type is retained during ion exchange and that the Li ions inserted into the structure occupy positions in close proximity to the original Na sites, though with a different coordination geometry (Figure S5) due to the significantly different sizes of the smaller Li ions. Further details about the fit procedure and the analysis of bond distances and atomic site valences calculated using bond valence sum (BVS) methods are provided in the Supporting Information (Figures S6 and S7a, Table S6). $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ was observed to be stable against both air and moisture exposure. Although $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ is a metastable phase, it does not decompose until heated to about 400 °C (Fig S7b).

Figure 3. Combined Rietveld refinement of synchrotron XRD data ($\lambda = 0.7788$ Å, top) and TOF neutron diffraction data (bottom) for $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ prepared by non-molten salt ion exchange. Experimental data are shown as black dots, the refined model as a red line, the difference curve in green, and the positions of Bragg diffraction peaks as purple tick marks.

Table 1. $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ atomic sites [P2_13 , $a = 9.11176(8)$].

Site*	x	y	z	$B_{\text{iso}} (\text{\AA}^2)$
Li1	0.05826(29)	0.05826(29)	0.05826(29)	2.93(22)
Li3	0.83101(34)	0.83101(34)	0.83101(34)	2.73(26)
Mg1	0.58095(7)	0.58095(7)	0.58095(7)	0.51(4)
Mg2	0.40120(8)	0.40120(8)	0.40120(8)	0.69(4)
P	0.09154(8)	0.26603(8)	0.34697(7)	0.58(3)
O1	0.00970(8)	0.88416(8)	0.21140(9)	0.79(3)
O2	0.00460(9)	0.13455(8)	0.39868(8)	0.73(3)
O3	0.19862(9)	0.32375(10)	0.46095(7)	0.83(3)
N	0.20307(6)	0.20307(6)	0.20307(6)	0.51(3)

*Wyckoff positions are either 4a (Li, Mg, N) or 12b (P, O)

The local structure of $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ was investigated by both neutron PDF and ^7Li MAS solid state NMR experiments. The PDF data for $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ (Figure S8) could be very effectively fit ($R_{\text{wp}} \sim 9\%$) using the average structural model from 1 – 20 $\text{\AA}$ when isotropic displacement parameters were used, suggesting that the local coordination environment is the same as the average coordination environment. The results of the PDF refinement (Table S7) do not significantly differ from the Rietveld refinement results. Similarly, no evidence for split sites was seen in ^7Li MAS NMR experiments, which showed only a single peak associated with Li ions at a chemical shift of -0.8 ppm (Figure S9). While this could be taken as evidence for rapid site exchange between the Li1 and Li3 sites, it is also very likely that the difference in chemical shifts between the Li1 and Li3 is too small to be resolved due to the diamagnetic nature of the sample. More comprehensive investigations will be required to determine if insights into the Li-ion mobility can be obtained from NMR experiments, efforts which are beyond the scope of the present work

The success of the Li^+/Na^+ ion exchange process indicates that both Li^+ and Na^+ ions can be mobile within this framework, though the timescale of this process will be limited by the ion with the lower mobility. Rough estimates of relative mobilities can be obtained by comparing percolation thresholds obtained in bond valence sum difference map calculations (Figure S10), with the structures obtained from the present neutron diffraction investigations used as input for these calculations. The 0.03 valence unit (v.u.) percolation threshold of Li in $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ is substantially lower than the 0.20 v.u. threshold of Na in $\text{Na}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$, suggesting that the Mg CUBICON framework is likely to have a higher Li^+ than Na^+ mobility, and that the Li ionic conductivity has a good chance of being high on an absolute scale.

Room temperature impedance spectroscopy data were therefore collected on dense ($\sim 92\%$) pellets of $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ using a custom-built measurement cell (Figure S11), and the data are shown in the form of a Nyquist plot in Figure 4. The EIS data were fit using an equivalent circuit consisting of two series elements of resistors paired with constant phase elements to model the bulk (R_b) and grain boundary (R_{gb}) resistances, with an additional constant phase element to describe the Warburg-like ionic conduction processes at low frequencies (Figure 4, top). Previous studies of CUBICON phases with redox-active transition metals (Fe, Ti)^{15, 35} have

found the electronic conductivity to be much lower (~ 2 orders of magnitude) than the ionic conductivity, and the ionic conductivity is expected to be even more dominant when the octahedral cation is Mg^{2+} . The electronic contributions to the measured conductivity were therefore neglected. A room temperature bulk ionic conductivity of $0.9 \times 10^{-6} \text{ S/cm}$ was inferred, a value which was comparable to the grain boundary resistance ($0.4 \times 10^{-6} \text{ S/cm}$), as is expected based on the similar sizes of their semicircular responses in the Nyquist plots. The ionic conductivity of $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ is greatly improved relative to that of $\text{Na}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$, as at 22 $^\circ\text{C}$ it is six orders of magnitude higher than that extrapolated for $\text{Na}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$.³⁶ Temperature-dependent EIS data for $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ were also collected using a protocol in which moisture was more rigorously excluded than for the room-temperature data, and comparable values for R_b and R_{gb} were obtained together with an activation energy of 0.44 eV based on a modified Arrhenius law fit (Figure S12, Table S8).

Figure 4. EIS data for $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ collected at 22 $^\circ\text{C}$ from 5 Hz to 13 MHz. Since features assigned to the bulk (b) and grain boundary (gb) contribution are well-resolved, an equivalent circuit was used in which their resistances (R_b and R_{gb}) were separately paired with constant phase elements (CPE_b and CPE_{gb}), together with a third constant phase element (CPE_l) which reflects the Warburg-like ionic conductivity of Li ions being perturbed by the electrolyte-electrode interface.

The room temperature Li-ion conductivity of $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ is intriguing with regard to applications as a solid state electrolyte. The measured room temperature ionic conductivity ($\sim 10^{-6} \text{ S/cm}$) is comparable to that of the well-known ionic conductor LiPON.³⁷ This value is about three orders of magnitude lower than the best oxide-based room temperature solid state Li-ion conductors discovered thus far^{8, 38-42}, but is comparable to the pre-optimization values of many of these systems. It is expected that the Li-ion conductivity of $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ can be substantially improved beyond the performance achieved in the present work by carrying out chemical substitutions that introduce persistent vacancies at the Li-ion sites, or which perturb the structural framework to make the motion of Li ions more facile. As such, this structural framework is an excellent starting point for designing fast Li ionic conductors for electrochemical storage applications. This system has the further benefit of having fully isotropic ionic conduction (due to its

cubic symmetry) and will be easier to work with in powder form than alternates with highly anisotropic conductivity. As

such, detailed structural studies into the ion exchange synthesis mechanism for this phase are merited.

Figure 5. Evolution of $\text{Li}_x\text{Na}_{2-x}\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ phases through four successive ion-exchange (IE) steps probed by lab XRD (Cu $K\alpha$).

3.2 *Ex situ* and *in situ* diffraction studies of ion exchange

Some initial insights into the mechanism of the ion exchange reaction which produces $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ were obtained from *ex situ* laboratory X-ray diffraction studies (Figure 5). It can be seen that two distinct phases are present in the intermediate stages of ion exchange, indicating that only a partial solid solution exists between $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ and $\text{Na}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ under these conditions. Whole-pattern Le Bail fitting (Figure S13) was effective when assuming that no more than two phases were present at each step, and the refined lattice parameters of these two cubic phases are presented in Table 2. The smaller Li-rich phase has essentially constant lattice parameters, while the cubic a -lattice parameter of the larger Na-rich phase decreases to 9.14 Å from an initial value of 9.25 Å (for pristine $\text{Na}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$) during ion exchange. It is therefore concluded that ion exchange begins through an initial solid solution pathway forming $\text{Li}_x\text{Na}_{2-x}\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ ($0 < x < 1$), beyond which there is no further Li solubility. Further Li exchange occurs through two-phase reaction mechanism in which the two phases are $\text{Li}_x\text{Na}_{2-x}\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ and $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$. The Na-rich phase has asymmetric diffraction peaks with a pronounced tail on the lower d -spacing side of the peaks (Figure S13 and S14). This is attributed to an asymmetrical lattice parameter distribution for the Na-rich phase due to a compositional gradient within crystallites, as can often be seen solid solution phases that are not fully equilibrated.

Table 2. Lattice parameter evolution during IE.

	Na-rich phase	Li-rich phase
Pristine	9.2467(1)	N/A
1 st IE	9.2348(2)	9.1191 (5)
2 nd IE	9.1487(9)	9.1154(2)
3 rd IE	9.1425(4)	9.1156(1)
4 th IE	N/A	9.1129(1)

Although *in situ* neutron diffraction studies of Li^+/Na^+ ion exchange have not previously been reported for any chemical system due to the challenging nature of such experiments, our development of non-molten salt exchange methods (which avoid the broad and high background of liquids) and the construction of time-of-flight neutron diffraction beamlines with good counting statistics offer the opportunity to for the first time follow the detailed structural changes that occur during ion exchange as they happen with good time resolution. The use of time-of-flight neutron diffraction allows excellent sensitivity to the changes in site occupancies and bond distances that occur during this transformation, especially for light elements (Li, Na, O, N) to which X-rays have weak sensitivity. While both $^7\text{LiBr}$ and $^7\text{LiCl}$ salts have sufficiently low neutron absorption cross-sections to be compatible with these experiments, $^7\text{LiCl}$ was utilized since it will be less absorbing during complementary X-ray diffraction experiments.⁴³

Figure 6. Schematic of *in situ* neutron diffraction experiments.

Figure 7. *In situ* neutron diffraction patterns collected during Li/Na ion exchange of $\text{Na}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ with the Miller indices of the Bragg diffraction peaks associated with CUBICON $\text{Li}_x\text{Na}_{2-x}\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ ($0 < x < 2$) labeled in black, LiCl ($\text{Li}_{1-y}\text{Na}_y\text{Cl}$) in pink, and NaCl ($\text{Na}_{1-z}\text{Li}_z\text{Cl}$) in green. Right panel shows a zoom of the (232) diffraction peak for $\text{Li}_x\text{Na}_{2-x}\text{Mg}_2\text{P}_3\text{O}_9\text{N}$. The temperature program is labelled on the right, with diffraction patterns at the beginning/end of ramps and at the middle of the hold highlighted in red.

Figure 8. Top: Evolution of lattice parameter (a) and phase fractions (b) for $\text{Na}_{2-x}\text{Li}_x\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ with $0 < x < 2$ (sodium-rich Phase A, blue) and $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ (Phase B, red) during ion-exchange. Bottom: Changes in Na-occupancy on the Na1 (c) and Na3 (d) site occupancy during the isothermal hold at 605 K. All results were obtained from Rietveld refinement using the *in situ* neutron diffraction data with experiment time as the horizontal axis.

The experimental configuration for *in situ* experiments used to more sensitively probe the ion exchange synthesis mechanism for $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ is schematically illustrated in Figure 6. Scans were collected every 0.5 h during an extended hold at 332 °C (605 K) of about 13 h, with somewhat longer collections during heating and cooling. The good quality of the *in situ* neutron diffraction data can be seen in the very clean diffraction patterns with peaks observable out to about 0.4 Å at 300 K and to 0.6 Å at 605 K (Figures 7, S15, and S16). Both sample peaks (labelled in black) and salt peaks (labelled in green for NaCl and purple for LiCl) are sharp with a sufficiently good signal/noise ratio to enable structural information to be accurately determined through Rietveld refinement. On heating, the $\text{Na}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ diffraction peaks shift to higher d spacing as a consequence of thermal expansion.

$\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ is first observed during the initial temperature ramp at about 525 K, indicating that the ion exchange process is quite rapid, especially since the $\text{Li}_x\text{Na}_{2-x}\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ solid solution must form prior to the appearance of $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$. Another signature of the onset of ion exchange is the asymmetry that appears in the LiCl peaks around 500 K, reflecting the formation of a partial $\text{Li}_{1-y}\text{Na}_y\text{Cl}$ solid solution with Na^+ lost from $\text{Na}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$, as can be seen in Figures S15 and S16. The formation of peaks associated with the reaction product NaCl (or a slight $\text{Na}_{1-z}\text{Li}_z\text{Cl}$ solid solution) does not occur before the isothermal hold, reflecting that NaCl does not form until sufficient Na ions are exchanged out of $\text{Na}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ to exceed solubility limit of Na^+ in LiCl. At the end of the *in situ* ion-exchange experiment, neutron diffraction data indicate the presence of four different coexisting phases in the reaction product: $\text{Li}_{1-y}\text{Na}_y\text{Cl}$, $\text{Na}_{1-z}\text{Li}_z\text{Cl}$, $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ and $\text{Li}_t\text{Na}_{2-t}\text{Mg}_2\text{P}_3\text{O}_9\text{N}$, where t is the solubility limit of Li^+ in this solid solution. It is not surprising that the ion exchange reaction does not run to completion since only a limited (4:1) molar excess of Li was used. On cooling at the end of the isothermal hold, the amount of $\text{Li}_x\text{Na}_{2-x}\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ decreases relative to that of $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$, indicating that a different equilibrium exists at lower temperatures. This shows that the width of the solid solution decreases at lower temperatures, as is expected based on thermodynamic arguments (less entropic stabilization). The *in situ* methods described here could also easily be adapted to rapidly map out the solubility limits as a function of temperature using a different temperature program.

The lattice parameters of the two CUBICON phases can be tracked throughout the ion exchange process. As shown in Figure 8a, the a lattice parameter of the sodium rich phase $\text{Li}_x\text{Na}_{2-x}\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ ($0 < x < t$) decreases monotonically as the reaction is held at constant temperature (605 K), though the rate of change slows by scan 30 (~18 h) and it appears that equilibrium is nearly achieved at the end of the isothermal hold (scan 35, ~21 h). In contrast, the lattice parameters of $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ do not significantly vary during the isothermal hold, supporting the assignment of this phase as a line compound. The relative mass fractions of these two phases were also followed through Rietveld refinement (Figure 8b), made possible by the high-quality diffraction data. It can be seen that about 20 wt% of $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ has already formed by the time the isothermal reaction temperature of 605 K is reached. The amount of $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ continues to increase (at the expense of the $\text{Li}_x\text{Na}_{2-x}\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ solid solution) until scan 20 (~14 h), after which the phase fraction remains essentially

constant during the isothermal hold. Surprisingly, this equilibration in phase fraction occurs well before the lattice parameters are equilibrated indicating that the reaction mechanism has unexpected complexity.

The refined occupancies of the Na1 and Na3 sites are shown in Figure 8c and 8d, and the behavior of these sites allows the origin of the complex reaction pathway to be understood. During the reaction, the occupancy of the Na1 site is seen to decrease from fully occupied (1.0) to about 0.6 by scan 20 (~14 h), but to then increase thereafter to a final occupancy which is again essentially fully occupied (1.0). In contrast, the Na3 site appears to remain fully occupied until scan 20 (~14 h), after which its occupancy decreases to about 0.3. While each individual data point has relatively large error bars (~0.1), the overall trend across many scans is very robust and indicates that substitution of Li^+ for Na^+ is initially most favorable near the Na1 site, but that as the cubic a lattice parameter shrinks with increasing substitution, there is a thermodynamic crossover and it becomes more favorable for Li to substitute near the Na3 site. The refined occupancies indicate that a higher degree of Li substitution can be tolerated at the Na3 site than on the Na1 site. It therefore appears that the range of $\text{Li}_x\text{Na}_{2-x}\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ solid solution compositions (Stage 1 of the transformation) should not be described as a single solid solution, but instead represents two thermodynamically distinct solid solutions phases (1a and 1b). This conclusion is further supported by the very different rates of change for many bond lengths between Stage 1a and Stage 1b (Figure S17).

3.3 Ion exchange synthesis mechanism

A detailed microscopic understanding of the local forces driving the two-part phase transition is made possible by the high quality structural data on intermediate phases provided by the *in situ* neutron diffraction experiments. The driving force for this complex behavior can be inferred from the changes in the volumes of the cation coordination polyhedra during the Li-exchange process (Figure 9a, Table 3). Even though the overall unit cell volume shrinks during the exchange of Li for Na, the volume of the local coordination polyhedron around Na1 increases when Li is partially substituted onto the Li1 site. In contrast, the volume of the Na3 coordination polyhedron always shrinks with Li substitution. As such, it is not surprising that it becomes more energetically favorable for Li to occupy the Li3 site than the Li1 site at higher degrees of Li substitution in which the cell volume is more significantly reduced from its original value due to the increasing strain caused by the volume expansion of the mixed Li1/Na1 site. It is this behavior which drives the non-monotonic behavior of the Na1 site occupancy. Intriguingly, this behavior of the Na1 site (increase in volume despite Na removal) is a likely reason for the exceptionally small volume changes (~0.5%) previously observed during the charging of $\text{Na}_3\text{TiP}_3\text{O}_9\text{N}$ batteries to form oxidized $\text{Na}_2\text{TiP}_3\text{O}_9\text{N}$,¹⁵ as Na removal during desodiation was shown through both experiment and theory to occur at the Na1 site during this process.

The limited stability range ($0 < x < 0.7$) of the $\text{Li}_x\text{Na}_{2-x}\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ solid solution observed during the *in situ* ion exchange experiments suggests that it is difficult for the cubic framework to simultaneously satisfy the bonding preferences of Li and Na in the mixed sites, leading to substantial

internal strains within the solid solution phases. A comparison of the local polyhedral volume changes with the volume change of the overall unit cell (Table 3, Table S9) shows that more than 90% of the overall unit cell volume reduction is accounted for by the changes in the cation local polyhedra for $\text{Li}_x\text{Na}_{2-x}\text{Mg}_2\text{P}_3\text{O}_9\text{N}$, while only 60% of the volume reduction in the line compound $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ occurs in local polyhedra. This is reflected in the strongly distorted MgO_6 octahedra present at the end of Stage 1a (Mg-O bond length spread of 0.60 Å; distortion indices of 0.117/0.041) relative to the very regular MgO_6 octahedra present in both end members, pristine $\text{Na}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ (bond length spread of 0.13 Å, distortion indices of 0.016/0.015) and fully lithiated $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ (bond length spread of 0.07 Å, distortion index of 0.006/0.013). Similarly, the mixed Na1/Li1 polyhedra in $\text{Li}_x\text{Na}_{2-x}\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ are larger than the Na1 polyhedron in the pristine material, while the pure Li1 polyhedron in $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ after ion exchange is smaller than the Na1 polyhedron in the pristine material. These strong local distortions highlight the energetic penalties for accommodating heterogeneous mixtures of Na and Li within this cubic framework, and based on these structural insights, it is not surprising that a full solid solution does not form between the end members of $\text{Na}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ and $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$.

Figure 9. (a) Representation (to scale) of the evolution of cation coordination polyhedral volume that occurs during ion exchange based on the structures obtained from in situ neutron diffraction

studies for the initial phase ($\text{Na}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$) and the phases at the end of Stage 1a ($\text{Li}_{0.4}\text{Na}_{1.6}\text{Mg}_2\text{P}_3\text{O}_9\text{N}$), Stage 1b ($\text{Li}_{0.7}\text{Na}_{1.3}\text{Mg}_2\text{P}_3\text{O}_9\text{N}$), and Stage 2 ($\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$). Polyhedral volumes (Å^3) are indicated, as are the distortion index of the MgO_6 octahedra. Additional comparative data are provided in Table 3. (b) Different patterns for changes in site occupancies that occur during Stage 1a (top) and Site 1b (bottom). Open circles indicate sites that are depopulated during each process. Additional details are given in Figure S19.

Table 3. Local and global volume changes (Å^3) during IE.

Polyhedron	Post-1a	Post-1b	Post-2
Mg1	-0.68	-1.55	-0.13
Mg2	-0.13	-1.32	-0.49
Na1/Li1	+2.25	+2.90	-2.59
Na3/Li3	-3.58	-4.78	-0.99
Sum over 4 sites	-2.14	-4.75	-4.20
¼ unit cell volume	-2.30	-5.24	-7.12

The reason why the variable composition $\text{Li}_x\text{Na}_{2-x}\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ phases represent two thermodynamically distinct solid solutions rather than a single solid solution is schematically illustrated in Figure 9b, with a more complete description of the pattern of site occupancies at each stage over the overall transformation provided in Figures S18 and S19. The first solid solution which is accessed during Stage 1a spans structures in which only three cation sites are utilized: Na1 (variable occupancy), Li1 (variable occupancy), and Na3 (constant occupancy). The second solid solution, accessed during Stage 1b, spans structures in which all four mobile cation sites (Na1, Li1, Na3, Li3) are utilized and have variable occupancies. Since these two solid solutions access different sets of atomic sites, they must belong to distinct and different thermodynamic phases. For comparison, the final two-phase reaction by which $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ is formed, Stage 2, involves a discontinuous reaction between the terminal solid solution composition of $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ (four mobile cation sites) and the simpler $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ end member, which only has two occupied mobile cation sites (Li1 and Li3). The $\text{Li}_x\text{Na}_{2-x}\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ solid solution is different from most other solid solution in that the variable content ions (Li and Na cations) do not occupy the same site, but instead occupy nearby sites which despite having the same site symmetry are clearly distinct as reflected in their different coordination numbers and very different bond lengths to the coordinating anions, thus permitting the extra phase transition.

The thermodynamic (and not kinetic) origin of the Stage 1a/1b crossover is supported by prior investigations into the diffusion pathways in this cubic framework, which indicate that both Na1 and Na3 sites must be traversed when Na ions move along the lowest energy diffusion pathway for this system, making both sites equally accessible.¹⁵ Further evidence for the thermodynamic nature of this transition is seen in behavior of the refined phase fractions. After stabilizing during the isothermal hold at 605 K, the fraction of the $\text{Li}_x\text{Na}_{2-x}\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ solid solution phase decreases during the subsequent sample cooling, suggesting that a different equilibrium is favored at lower temperatures and that the time scale of equilibration is relatively fast. It is generally expected that

the compositional width of solid solutions will decrease as temperature is lowered since the entropic stabilization of the mixed phase relative to its ordered alternatives will be lessened, and the present *in situ* neutron diffraction data do indeed show this expected behavior, as seen in Figure 8b. In fact, the equilibrium constants for this system could rapidly be determined by collecting additional *in situ* diffraction data with a different temperature program including holds to equilibrate the system at multiple temperatures, illustrating another valuable capability of *in situ* methods.

4. Conclusions

In the present work, metastable $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ was for the first time synthesized from $\text{Na}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ using a non-molten salt ion exchange method. The room temperature Li-ion conductivity of $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ is found to be almost 10^{-6} S/cm, a value that is comparable to LiPON. The non-molten salt synthesis method was exploited to carry out the first-ever *in situ* neutron diffraction study of Li/Na ion exchange, which allowed the collection of quality structural data with modest counting times (~30 min steps) even at elevated temperatures (~300 °C). Although the lattice parameters decrease monotonically across the partial $\text{Na}_{2-x}\text{Li}_x\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ solid solution that forms for small degrees of ion exchange, a hidden phase transition can be resolved in Rietveld refinements against the *in situ* neutron diffraction data. The second phase transition within the solid solution is associated with the different patterns of site occupancies in the early and late stages of this solid solution. This novel approach of using a solid rather than a liquid source of ions for the exchange reaction is generally applicable to *in situ* mechanistic studies for characterizing solid state compounds with mobile ions, and opens important new routes to understanding and improving materials for energy storage applications.

ASSOCIATED CONTENT

Supporting Information. X-ray and neutron diffraction data and structure refinement parameters for $\text{Na}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$, $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$, Fourier difference maps showing Li site positions, neutron PDF and ^7Li NMR studies of $\text{Li}_2\text{Mg}_2\text{P}_3\text{O}_9\text{N}$ *in situ* neutron diffraction patterns, impedance spectroscopy data, and additional schematic models of structures and phase transitions. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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