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Insights into the Fast Sodium Conductor NASICON and the Effects of Mg^{2+} Doping on Na^+ Conductivity

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ABSTRACT: Na super ionic CONductor (NASICON), $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$, is an excellent solid-state electrolyte on account of its high sodium-ion conductivity, which can be further enhanced through chemical doping. However, the underlying sodium diffusion mechanism and how it is affected by chemical doping are not fully understood. This, in part, stems from the ambiguity between reported average structure models, where there is variation in the number and location of the sodium crystallographic sites. In this work, we present a neutron scattering study on monoclinic NASICON and Mg^{2+} -doped NASICON, with a focus on the characterization of the sodium sites. Our difference Fourier maps show that the sodium sites have limited long-range order at temperatures as low as 3 K. In addition, our characterization of Mg^{2+} -doped NASICON suggests that although Mg^{2+} preferentially dopes the secondary Na_3PO_4 phase rather than the bulk NASICON phase, its NASICON sodium sites are comparatively more diffuse. Furthermore, quasi-elastic neutron scattering data show broader spectra for the Mg-doped NASICON compared to NASICON at 300 K, supporting a more dynamic environment. We propose that the more diffuse character of the sodium sites arising from the introduction of Mg^{2+} contributes to the improvement of ionic conductivity in Mg-doped NASICON near room temperature.

■ INTRODUCTION

The NASICON (Na super ionic CONductor) family of compounds, with general formula $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ ($0 < x < 3$), is a class of sodium ionic conductors that has gained prominence as a promising sodium solid-state electrolyte material on account of its high ionic conductivity as well as excellent air and moisture stability.^{1–4} Significant variations in the total ionic conductivity result from tuning x , with the highest value reported for $x \approx 2.0$ ($\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_4$), where the material crystallizes in a monoclinic structure, with space group C2/c .^{1,5}

A key feature of NASICON is its skeletal framework structure formed by alternating corner-sharing ZrO_6 octahedra and Si/PO_4 tetrahedra. These form a three-dimensional linked interstitial space, which facilitates fast sodium-ion conduction. Numerous studies on NASICON's structure show excellent agreement on this framework structure. However, there has been considerable debate concerning the number, position, and occupancies of the sodium sites included in the average structure model. Moreover, difficulties in growing a single crystal of NASICON in the monoclinic phase and the dependence of the final sodium content on the method(s) used to synthesize samples have contributed to the lack of clarity in reaching an unambiguous crystal structure solution.^{1,6,7} This has resulted in various studies reporting crystal structure models for the same composition of NASICON that include three sodium sites,^{1,8,9} four sodium sites^{7,10} and most recently, five sodium sites.¹¹

Clarity on this point is desirable to better understand ionic conduction in NASICON.

While NASICON has demonstrated its potential as a solid-state electrolyte material, its total ionic conductivity is hampered by the effects of grain boundaries and impurity phases.⁴ Chemical doping is one strategy that has been widely used to address this issue.^{3,4,12,13} In the case of Mg^{2+} doping, it has been shown that the total ionic conductivity was improved from the order of 0.01 mS/cm in the parent NASICON (no chemical doping) to 2.71 mS/cm for composition $x = 0.128$ in $\text{Na}_{3+2x}\text{Zr}_{2-x}\text{Mg}_x\text{Si}_2\text{PO}_{12}$.⁴ Previous work¹² has suggested that Mg^{2+} substitutes the Zr^{4+} site, given that these species have the same ionic radius (0.72 Å) in 6-fold coordination.¹⁴ However, computational work by Samiee et al.⁴ suggests Mg^{2+} preferentially dopes the secondary impurity Na_3PO_4 phase rather than the expected Zr^{4+} site in the bulk NASICON phase. To understand the overall improvement in ionic conductivity, it is necessary to examine both the location of the primary Mg^{2+} doping site and what effect, if any, this has on the sodium dynamics in NASICON.

Table 1. Summary of the Positions and Site Occupation Factors of the Sodium Sites from the Three Average Structure Models Tested in This Work

model	Na site label	Wyckoff site	x	Y	z	site occupancy factor
3 Na model ⁸	Na1	4d	0.25	0.25	0.5	0.81
	Na2	4e	0.5	0.891	0.25	1.0
	Na3	8f	0.836	0.079	0.842	0.6
4 Na model ⁷	Na1	4d	0.25	0.25	0.5	0.2301
	Na2	4e	0	0.1081	0.25	1.0
	Na3	8f	0.3271	0.0779	0.3099	0.5455
	Na4	8f	0.3179	0.1408	0.4382	0.4022
5 Na model ¹¹	Na1	4d	0.25	0.25	0.5	0.24
	Na2	4e	0	0.405	0.25	0.88
	Na3	8f	0.3386	0.42649	0.34625	0.38
	Na4	8f	0.193	0.118	0.574	0.44
	Na5	8f	0.75826	0.48129	0.94726	0.12

Figure 1. Rietveld refined fit of the (a) 3 Na model (starting model from Baur et al. (1986)), (b) 4 Na model (starting model from Boilot et al. (1987)), and (c) 5 Na model (starting model from Zhang et al. (2019)) to the 3 K NPD pattern ($\lambda = 1.6215(5)$ Å). The data are shown as black crosses, the calculated Rietveld model as a red line through the data, and the difference between the data and the model as the blue line below. Reflection markers for monoclinic NASICON, γ - Na_3PO_4 , and ZrO_2 are shown in magenta, cyan, and black, respectively.

This work focuses on monoclinic NASICON and is presented in two parts. In the first section, we present the structural characterization of pure monoclinic NASICON, with a focus on the number and crystallographic positions of the sodium sites in a neutron powder diffraction study. In the second section, we present a focused study on Mg^{2+} -doped NASICON ($\text{Na}_{3+2x}\text{Zr}_{2-x}\text{Mg}_x\text{Si}_2\text{PO}_{12}$). Exploration of the Mg^{2+} doping site and the effect this has on sodium location and dynamics in

NASICON was conducted using a combination of neutron powder diffraction and quasi-elastic neutron scattering.

EXPERIMENTAL SECTION

Powder samples of $\text{Na}_{3+2x}\text{Zr}_{2-x}\text{Mg}_x\text{Si}_2\text{PO}_{12}$, with target compositions $x = 0, 0.032, 0.064$, and 0.128 were prepared *via* a solid-state reaction as follows. Stoichiometric amounts of Na_2CO_3 (Fisher Scientific, 99.5%), ZrO_2 (Fisher Scientific, laboratory grade), SiO_2 (Alfa Aesar, 99.9%),

$\text{NH}_4\text{H}_2\text{PO}_4$ (Sigma-Aldrich, 99.99%), and MgO (Alfa Aesar, 99.95%) were ball milled with isopropanol for 24 h. The mixture was subsequently dried at 85 °C for 8 h before being sintered at 1150 °C for 5 h. After the sample cooled, it was ground with an agate mortar and pestle.

High-resolution neutron powder diffraction (NPD) patterns of all samples were measured on Echidna^{14,15} at the Australian Nuclear Science and Technology Organisation (ANSTO). The powders were packed in 9 mm diameter vanadium cans and measured at 3, 100, 200, 300, and 400 K using a wavelength of 1.6215(5) Å. Additional patterns at 100, 200, 300, and 400 K were measured on all samples using a wavelength of 2.4395(5) Å. For all collected patterns, the structures of the respective samples were modeled *via* Rietveld analysis using GSAS/EXPGUI.^{16,17}

Quasi-elastic neutron scattering (QENS) experiments were performed on the high-resolution backscattering spectrometer Emu¹⁸ at ANSTO on $\text{Na}_{3+2x}\text{Zr}_{2-x}\text{Mg}_x\text{Si}_2\text{PO}_{12}$ for the $x = 0$ and 0.128 compositions. The powder samples were packed into 22.5 mm diameter aluminum sample cans. Inelastic spectra of both samples were measured at 200, 300, and 400 K over an energy range ± 31 μeV at a final wavelength of 6.27 Å. The inelastic spectrum measured on the $x = 0$ composition at 2 K was used as the resolution function. The inelastic spectrum measured on a standard vanadium cylinder was used for detector efficiency and solid-angle corrections. An empty sample can was similarly measured at 2, 300 and 400 K for background subtraction.

RESULTS AND DISCUSSION

The ionic conductivities of Mg-doped NASICON ($\text{Na}_{3+2x}\text{Zr}_{2-x}\text{Mg}_x\text{Si}_2\text{PO}_{12}$) coupled with theoretical calculations were previously reported.⁴

Investigation on the Nature of the Na Sites Using NPD.

The relative merits of including 3,⁸ 4,⁷ or 5¹¹ sodium sites in the model of the average structure were assessed via Rietveld analysis of the NPD data collected at 3 K. The rationale for using the 3 K data is that it provides a representative view of monoclinic NASICON when all sodium sites are effectively ‘frozen’ onto their crystallographic positions. It is of interest to note that the additional sodium sites included in the 4- and 5-sodium site models are positioned along the interstitial channel between the 3-sodium site model. Hence, comparing the fits of these models to our data provides insight into whether it is necessary to include these additional crystallographic positions in the average structure model or if the ambiguity surrounding the number of sodium sites is an indication of the limited observable long-range order of sodium in NASICON. Clarity on this point would also provide a platform for future work on modeling the microscopic sodium diffusion mechanism.

Table 1 summarizes the positions and site occupancy factors of the sodium sites from the three average structure models tested in this work. Rietveld refined fits of the three models are shown in Figure 1, and the crystallographic details are summarized in Tables S2–S4 in the Supporting Information. Care was taken with considering the sodium site occupancies factors (SOFs), and these were fixed to the values found in the literature. Freely refining SOFs lead to unstable refinements; however, refining only the sodium SOFs at the end of the refinements presented in Figure 1 and Tables S2–S4 leads to the values reported in the Supporting Information Tables S5–S7 with the statistics of these fits presented in Table S8. Overall, it appears that the total sodium amount is underestimated in the cases of the 3- and 4-sodium site model, while it is on par with the 5-sodium site model. Nonetheless, the difference in the goodness of fit between the 3- and 5-sodium site models is marginal at best. The sample was also found to include secondary phases $\gamma\text{-Na}_3\text{PO}_4$ and ZrO_2 (wt. fractions 3 and 8%,

respectively). As shown, all three NASICON models fit the 3 K data well, with only small differences in the fit residuals and quality of fit, as reflected in the fit statistics (Table 2). This

Table 2. Summary of the Fit Statistics from the Rietveld Refined Fits of the Three NASICON Models to the 3 K NPD Data

model	χ^2	R_p (%)	wR_p (%)
3 Na model	1.72	2.35	2.98
4 Na model	1.96	2.70	3.39
5 Na model	1.71	2.31	2.96

suggests that all three models are plausible descriptions of the average structure and that, within the sensitivity of our measurement, there is no clear benefit in the inclusion of sodium sites beyond those characteristic of the 3 Na model. A number of ADPs appear either comparatively larger (e.g., Na1) or smaller (e.g., O1) than expected, Table S2. Various tests were applied to check the robustness of the model. In particular, the Na1 ADP was fixed to the smaller value of the Na3 ADP, and Na atomic positions and SOFs refined. This was then followed by the refinement of the Na ADPs. The fit statistics and structural tables are presented in Tables S9 and S10. Although the fit statistics are similar, there is an underestimate of the Na concentration, and the atoms with either large or small ADPs remain.

Since the relative merits of the models could not be easily ascertained in our Rietveld analysis, difference Fourier maps were used to gain additional insight into the nature of the sodium sites with minimal model bias. These maps (Figure 2) were generated from a fit of the NASICON framework structure to the NPD data (i.e., all sodium occupancies set to zero). In this way, regions in the maps that show high nuclear density correspond to the location of sodium. Comparing the difference Fourier map at 3 K with the reported crystallographic positions from Hong’s seminal work,¹ there are features that could correspond to additional sodium sites. The nuclear density around the Na3 sites also appears diffuse at 3 K. Interestingly, as the temperature increases to 400 K, the maps indicate that both the Na1 and Na3 sites localize onto the reported crystallographic positions in the 3 Na model. By contrast, the population of the Na2 site, which is also the only fully occupied sodium site in the average structure model, follows the expected behavior of being comparatively more diffuse at 400 K than at 3 K. This suggests a possibility that sodium in sites that are included as partially occupied sites in the average structure model could migrate to a preferred crystallographic position with increasing temperature.

Effect of Mg^{2+} Doping on NASICON. Insight into the Mg^{2+} doping site was gained by examining the dependence of the lattice parameters of $\text{Na}_{3+2x}\text{Zr}_{2-x}\text{Mg}_x\text{Si}_2\text{PO}_{12}$ as a function of Mg concentration. Substitution of the Zr^{4+} site in the NASICON phase is expected to result in a larger bottleneck diameter and, consequently, the expansion of the cell volume. On the other hand, if doping of the $\gamma\text{-Na}_3\text{PO}_4$ phase is preferred, this is expected to result in substitution on the Na^+ site(s) in $\gamma\text{-Na}_3\text{PO}_4$ and consequently, a contraction in the total cell volume of $\gamma\text{-Na}_3\text{PO}_4$. Figure 3 shows the NPD patterns of $\text{Na}_{3+2x}\text{Zr}_{2-x}\text{Mg}_x\text{Si}_2\text{PO}_{12}$ for $x = 0, 0.032, 0.064$, and 0.128, which were measured at 300 K using a wavelength of 2.4395(5) Å. As shown, there is little to no perceivable change in the positions of the reflections from the NASICON phase, while the 111 reflection of the $\gamma\text{-Na}_3\text{PO}_4$ phase shows an observable shift

Figure 2. Visualization of the effect of increasing temperature on the sodium sites as viewed from slices across the 100 plane of Fourier difference maps generated from setting the Na occupancy to zero in the fit of the 3 Na model to the NPD data of NASICON. The color scale for the Fourier difference maps shows regions with the greatest difference between the model and data in red and the least difference in blue. The O and P/S sites that have a small proportion of the intensity on these lattice planes have been removed for the structural model shown on the left for clarity.

to a higher scattering angle, indicating a lattice contraction with increasing Mg^{2+} concentration. The same effect is observed in XRD patterns of the same samples, which are shown in Figure S7 in the Supporting Information.

The possibility of Mg^{2+} substitution on the Zr^{4+} site was also considered based on the identical ionic radii for these species of 0.72 Å in 6-fold coordination.¹⁹ The $x = 0.128$ case at 300 K with both wavelengths of NPD data is used as a demonstration as it contains the highest amount of Mg. Briefly, 5%, 10%, and all of the Mg was placed on the Zr site and the structural model refined. Furthermore, refinement of the Mg:Zr ratio on the nominally Zr site was also conducted. The structural tables are presented in Tables S11–S14, a comparison of the refinement statistics in Table S15, and the variation in the bond valence sum (BVS) of the Zr site with the different occupation in Table S16. There is very little change in the statistics of the fit among the models, but more importantly, the BVS in each case is 4 for the Zr site, and the refined ratio put within error 0 Mg on the Zr site. It should be noted that in this case, BVS is more sensitive to Mg:Zr ratio than NPD as the contrast in the neutron scattering lengths is only ~33% (5.375 vs 7.16 fm) compared to the contrast of 200% in oxidation states +2 vs +4. Bearing this in mind, the model with no Mg:Zr was used, but some Mg:Zr substitution or similar cannot be fully ignored with the current data. Bond valence sums (BVS) of the refined models (no Mg in the model) at 300 K with both wavelengths of NPD data for all samples are presented in Table S17. The Zr sites equate to 4, and the Na2 and Na3 sites equate to ~1. The Na1 and the P1/Si1 and P2/Si2 sites are underbonded based on BVS considerations.

Rietveld refined fits to the NPD patterns (see Figures S2–S4 in the Supporting Information) showed that the cell volume of the NASICON phase had a small expansion in the total cell volume. However, this change is minimal in comparison to the contraction in the cell volume of the $\gamma\text{-Na}_3\text{PO}_4$ phase (Figure 4). This indicates that, at all temperatures, although some Mg^{2+} could be substituting for Zr^{4+} in the NASICON phase, the $\gamma\text{-Na}_3\text{PO}_4$ phase is preferentially doped. Clearly, Mg^{2+} substitutes in the Na_3PO_4 phase, which has been thoroughly investigated in terms of structure and dynamics recently,²⁰ but this substitution

may result in extra sodium for the NASICON phase (i.e., expelled from Na_3PO_4 if the weight fractions are constant with doping levels). However, the current data does not have the sensitivity to quantify this amount, as indicated by the refinements of the Na SOFs, which typically were not very stable. Furthermore, the weight fractions of the samples are tabulated in Table S18, showing a stable ZrO_2 impurity content but increasing Na_3PO_4 content. This suggests that the Na_3PO_4 “uses” more Na with higher levels of doping based on the weight fraction increase.

Despite the indication that the Mg^{2+} predominantly dopes Na_3PO_4 , there is still some suggestion of a qualitative change in the nature of the sodium sites in the bulk NASICON phase. Difference Fourier maps were generated from fits of the average structure model with all Na occupancies set to zero to the NPD data at 300 K (Figure 5). These maps indicate that sodium in the doped NASICON samples is more diffuse than in the parent material. Moreover, there is a suggestion of site splitting in the direction of the interstitial channels, forming a possible diffusion pathway through the structure. These appear to connect with each other across multiple unit cells (Figure 5b), which could rationalize part of the increase in total ionic conductivity in the Mg^{2+} doped samples.

Further indications of the effect of Mg^{2+} doping on sodium in NASICON are observable in the QENS measurements conducted on $\text{Na}_{3+2x}\text{Zr}_{2-x}\text{Mg}_x\text{Si}_2\text{PO}_{12}$ for the $x = 0$ (parent sample) and $x = 0.128$ compositions. Here, a detailed analysis of the Q -dependence of the QENS spectra was not undertaken. However, a qualitative comparison between the parent and Mg-doped samples can be drawn from the scattering function summed over all detectors, excluding those that coincide with Bragg peaks. As shown in Figure 6, the QENS broadening of the Mg-doped sample is greater than that of the parent sample at 300 K. This suggests that the Mg^{2+} doping effectively both lowers the activation energy required for sodium diffusion in NASICON and increases Na^+ conductivity at ambient temperature. This result is consistent with electrochemical impedance measurements reported in Samiee et al.,⁴ which showed significantly higher room temperature ionic conductivity of

Figure 3. (a) NPD patterns ($\lambda = 2.4395(5)$ Å) of $\text{Na}_{3+2x}\text{Zr}_{2-x}\text{MgSi}_2\text{PO}_{12}$ for $x = 0, 0.032, 0.064$, and 0.128 at 300 K. (b) Close-up of the (111) reflections of the NASICON and γ - Na_3PO_4 phases for the same patterns. The reflections for the phases are labeled in black and red, respectively.

Figure 4. Effect of varying the Mg^{2+} doping concentration on the cell volume of the NASICON and γ - Na_3PO_4 phase at 300 K.

Figure 5. Difference Fourier maps showing four unit cells (each cell shown by the black outline) at 300 K. The Fourier density representing the distribution of sodium in (a) neat NASICON and (b) Mg^{2+} -doped NASICON is shown in yellow. Note, the same scattering density intensity cut-off was used for both maps.

Mg -doped NASICON in comparison to the parent material. Interestingly, further increases in the QENS broadening of the Mg -doped sample at 400 K are small in comparison to the parent sample. The difference in the temperature dependence of the two samples could suggest that the sodium diffusion processes in the two samples are different; however, further studies are required for an in-depth characterization.

CONCLUSIONS

This work has shown that sodium in monoclinic NASICON has limited observable long-range order even at temperatures as low as 3 K. The distribution of sodium along the interstitial channels of the framework structure could account for one contribution to the inherent high ionic conductivity of NASICON, in addition to the wide interstitial channels formed by the skeletal framework structure. Our study also suggests that increasing the temperature causes sodium to migrate to preferred crystallographic positions. The combination of these two factors is a possible explanation for the ambiguity in defining the sodium sites in the average structure model.

From our characterization of Mg^{2+} -doped NASICON, there is strong evidence that Mg^{2+} preferentially dopes the secondary γ - Na_3PO_4 phase rather than the bulk NASICON phase. Despite this, our difference Fourier maps suggest that the minimal Mg^{2+} doping causes the sodium in NASICON to be comparatively more diffuse than in the parent material, which could contribute

Figure 6. Comparison of the difference in QENS broadening as a result of Mg^{2+} doping at (a) 300 K and (b) 400 K as viewed from the summed scattering function $S(\omega)$.

to the lower activation energy required for sodium diffusion. This is supported by our preliminary QENS data, where broader spectra were observed for the Mg-doped NASICON sample in comparison to the parent sample at 300 K.

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All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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