Phase Behavior in NaSiCON Electrolytes and Electrodes

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Abstract

The replacement of the presently used liquid electrolytes by a non-flammable solid electrolyte is an important avenue to create safer batteries. The Sodium Superionic CONductor (NaSiCON) $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ ($0 \leq x \leq 3$) that displays high bulk ionic conductivity and good stability towards other NaSiCON-based electrodes is a good solid electrolyte in NaSiCON-based batteries. Despite the sizeable share of research on $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$, the structural and thermodynamic properties of NaSiCON require better understanding for more efficient synthesis and optimization as a solid electrolyte, which often follows chemical intuition. Here, we analyze the thermodynamic properties of the NaSiCON electrolyte by constructing the $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ phase diagram, based on density functional theory calculations, a cluster expansion framework, and Monte Carlo simulations. Specifically, we build the phase diagram as a function of temperature and composition ($0 \leq$

$x \leq 3$) for the high-temperature rhombohedral structure, which has been also observed in several positive electrode materials, such as $\text{Na}_3\text{Ti}_2(\text{PO}_4)_3$, $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, $\text{Na}_3\text{Cr}_2(\text{PO}_4)_3$, and $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$. Through the phase diagram, we identify the concentration domains providing the highest Na^+ -ion conductivity and previously unreported phase-separation behavior across three different single-phase regions. Further, we note the similarities in the phase behavior between $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ and other NaSiCON-based mono-transition metal electrodes and discuss the potential competition between thermodynamics and kinetics in experimentally observed phase separation. Our work is an important addition in understanding the thermodynamics of NaSiCON-based materials and in the development of inexpensive Na-ion batteries. From our results we propose that the addition of SiO_4^{4-} moieties to single-transition metal NaSiCON-phosphate-based electrodes will slow significantly the kinetics toward phase separation.

1 Introduction

The development of green energy technologies, such as photovoltaics, wind turbines and rechargeable batteries, is essential in meeting the sustainable needs of a society to limit its fossil fuel usage. Lithium (Li)-ion batteries power the world’s mobile devices, and they are increasingly seen in vehicular transportation. When life-cycle analysis is examined in the design of batteries, however, sodium (Na) appears attractive since it can be “harvested” directly from seawater, making Na $\sim$ 50 times lower in cost than Li.^{1–3} Na-ion batteries also use inexpensive, stainless-steel current collectors.² However, commercial Li-ion batteries and the state-of-the-art Na-ion batteries employ highly flammable organic liquid electrolytes,^{4,5} which pose a tangible safety concern in their widespread deployment.

A pathway to create a battery with a high energy density as well as safety is to replace the liquid with a non-flammable solid electrolyte,⁶ leading to all-solid-state batteries, which are the object of a sizeable amount of current research.^{7–24} Today, the super-ionic conductivity of Li^+ and Na^+ -ions in solid electrolytes can achieve record-values $> 10 \text{ mS}\cdot\text{cm}^{-1}$ at room temperature,^{25–27,27} rivalling those of commercial liquid electrolytes (e.g., 1 M LiPF_6 in dimethyl/ethylene carbonates $\sim 10^{-2} \text{ S}\cdot\text{cm}^{-1}$).²⁸ More than 40 years ago, Hong and Goodenough studied the “Sodium Superionic CONductor” (NaSiCON), $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ ($0 \leq x \leq 3$),^{29,30} which can achieve exceptional bulk ionic Na^+ -conductivity ($\sim 15 \text{ mS}\cdot\text{cm}^{-1}$ at 298 K) for $x \sim 2.0\text{--}2.4$.³¹ The NaSiCON structure provides a versatile framework, incorporating both cationic (Na^+ and Zr^{4+}) and anionic (SiO_4^{4-} and PO_4^{3-}) moieties,^{32,33} which enable the number of Na^+ -ions to vary between 1 and 4 per formula unit with corresponding changes in the P:Si ratio and Na^+ -ion conductivity.

Figure 1 depicts the structure of the high-temperature ($> 450 \text{ K}$) rhombohedral (space group: $R\bar{3}c$) phase of $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$,^{29,30,32,33} where the 3 blue XO_4 ($\text{X} = \text{P}$ or Si) tetrahedra share corners with two grey ZrO_6 oc-

tahedra forming the so-called “lantern units” (panels **a** and **b**). There are two distinct, partially occupied (disordered) sodium sites, Na(1) and Na(2) (panel **b**). The super-ionic behavior in $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ is driven by a Na-vacancy migration mechanism that relates directly to the occupational disorder of Na(1) and Na(2).^{29,34–36} The Na(1) site is typically larger than Na(2) and is coordinated by oxygens atoms from ZrO_6 units in an anti-prismatic arrangement (Figure 1**b** and 1**c**), while Na(2) resides in an irregular polyhedral, coordinated to seven neighboring oxygen atoms from the ZrO_6 and XO_4 units. The existence of a third Na site between Na(1) and Na(2) has been reported,^{33,37} and attributed to a metastable state in the Na^+ migration. At lower temperatures ($< 450 \text{ K}$) and for $1.8 \leq x \leq 2.2$ for x in $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$, the NaSiCON undergoes a monoclinic distortion (space group: $C2/c$) that is often associated with Na^+ ordering into distinct Na sites and lower Na-conductivities.²⁹ Here, we will use the nomenclature rhombohedral- and monoclinic-NaSiCON to distinguish the two $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ phases.

There exists an extensive body of prior literature on optimizing the Na-ion conductivity within the NaSiCON electrolyte,^{30,31,33,34,36–40} especially at $x \sim 2$ in $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$. Aliovalent doping has been used to increase the Na-ion conductivity by varying the Na content and disorder in NaSiCON.^{34,38–40} For example, Miyajima et al.⁴¹ studied the partial substitution of Zr^{4+} by 3+ cations, such as In^{3+} , Yb^{3+} , Er^{3+} , Y^{3+} , Dy^{3+} , Tb^{3+} , and Gd^{3+} in $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ leading to an increase of the Na content. While Sc^{3+} has also been used as a common aliovalent dopant on Zr^{4+} ,^{39–41} high Na^+ conductivities ($\sim 3.7 \text{ mS}\cdot\text{cm}^{-1}$) have been achieved by doping with trivalent Al^{3+} , Fe^{3+} , and Y^{3+} , and divalent Co^{2+} , Ni^{2+} , and Zn^{2+} species.³⁸ The complete substitution of Zr^{4+} in NaSiCON by redox-active transition metals,^{36,38–40} e.g., Ti, V, Cr, and Fe, in NaSiCON transforms the solid electrolyte into an electrode. Notably, NaSiCON-derived electrodes (e.g., $\text{Na}_3\text{Ti}_2(\text{PO}_4)_3$, $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ and $\text{Na}_3\text{Cr}_2(\text{PO}_4)_3$) often show

Figure 1: Representation of the rhombohedral $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ structure. Na(1) is represented by red anti-prisms or red spheres, Na(2) by silver spheres, (Si/P) O_4 by blue tetrahedra and ZrO_6 by grey octahedra. Panel a shows the lantern arrangement, whereby Na(1) positions are stacked between two ZrO_6 octahedra along the [001] direction. Panel b depicts a zoomed view (of panel a) of the Na(1) and Na(2) arrangement within the rhombohedral cell. Panel c shows a view down the c -axis.

phase-separation behavior upon Na intercalation/extraction.^{34,42,43,43–47}

The phase behavior –phase separation or the existence of solid solutions– has not been fully elucidated in $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$. Specifically, the experimentally observed disorder and fractional occupancies of the Na/Vacancy (Va) and Si/P sites in the rhombohedral-NaSiCON structure^{29,30,33} hinder characterization attempts in assigning specific phases (or ordered Na configurations) at different temperatures and Na compositions. In this investigation, we therefore analyze the phase behavior of the NaSiCON electrolyte by constructing the $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ phase diagram as a function of composition ($0 \leq x \leq 3$) and temperature. We focus on the high-temperature rhombohedral-NaSiCON $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ structure, which exhibits high Na-conductivity and is adopted by several Na-based positive electrodes (e.g., $\text{Na}_3\text{Ti}_2(\text{PO}_4)_3$, $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, $\text{Na}_3\text{Cr}_2(\text{PO}_4)_3$ and $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$) as well at

high temperature. The phase diagram is developed by grand canonical Monte-Carlo (GCMC) simulations based on a cluster expansion (CE) model,⁴⁸ which is built on density functional theory (DFT)^{49,50} calculations. Importantly, we find specific temperature and Na-concentration domains where the rhombohedral-NaSiCON exhibits a biphasic behavior (or phase separation), which is similar to the behavior observed in NaSiCON-based electrodes. Finally, we provide strategies for further optimizing the synthesis of NaSiCON-related materials and improving their ion-transport properties.

2 Details of Monte Carlo, Cluster Expansion and DFT Calculations

To coarse grain the Gibbs free-energy with changes in composition and temperature of the rhombohedral $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$, the Metropolis-Hasting GCMC⁵¹ was performed using a CE Hamiltonian. The CE was parameterized on various Na-vacancy (Va) and Si-P configurations, and the CE fit was obtained using the cluster assisted statistical mechanics (CASM) code.^{52–55} In performing the GCMC simulations, every Na/Va swap must be coupled to a Si/P swap or vice versa, in order to maintain the charge neutrality of the overall simulation cell. We have enforced the charge neutrality by modifying the GCMC code in the CASM package (<https://github.com/caneparesearch/CASMcode>).^{52–55} GCMC runs were performed on $16 \times 16 \times 16$ supercells of the primitive cell with 172,032 atoms and ranged between 57,344,000 and 573,440,000 steps. The condition of charge neutrality increases substantially the number of GCMC steps required to achieve convergence compared to GCMC simulations without this constraint. GCMC simulations were considered converged when deviations in formation energies reached ≤ 0.5 meV/f.u.

In GCMC, either the chemical potential (μ) or temperature (T) can vary. Due to the charge-

neutrality constraint, there is a single independent μ in the NaSiCON system, i.e., one unique composition variable (x). As a result of the three ground-states in the convex hull at $x = 0, 2$ and 3 (see Section 3.1), μ was scanned in two regions with a fine step-size ($\Delta\mu = 0.005$ eV/f.u) in both “forward” and “backward” directions (Section S4 in Supporting Information, SI). GCMC scans were also performed at fixed μ and with varying T from 5 to 1605 K ($\Delta T = 5$ K).

The CE Hamiltonian, based on the approach of Sanchez et al.,⁴⁸ parameterizes the formation energies (E_f in Eq. 2), as calculated from DFT, of various Na/Va and Si/P configurations, which are mapped onto a fixed $\text{Na}_4\text{Zr}_2\text{Si}_3\text{O}_{12}$ topology. The CE is typically written as a truncated summation of the Effective Cluster Interactions (ECIs) of pair, triplet, quadruplet, and higher order clusters as:

$$E[\vec{\zeta}, \vec{\phi}] = V_0 + V_i \zeta_i + V_{ij} \zeta_i \zeta_j + V_{ia} \zeta_i \phi_a + V_{ab} \phi_a \phi_b + \dots \quad (1)$$

where $E[\vec{\zeta}, \vec{\phi}]$ is the formation energy of a Na/Va and Si/P configuration (i.e., a given structure). The ECI V , and a polynomial function mapping the occupation of the lattice site, with $\zeta_i = 0$ or 1 representing the occupation of Na or Va and $\phi_a = 0$ or 1 that of Si or P.⁵⁶ Each ECI in the sum includes the multiplicity (the cluster symmetry). All symmetrically distinct pairs, triplets, and quadruplets in the rhombohedral cell within a radius of 10 Å, 6 Å and 5 Å, respectively, are used for constructing the CE model. Note that including larger clusters via increasing the maximum radius (within which clusters are included) results in a dramatic increase of the basis-set size and the complexity of the fitting procedure, without any improvement in the quality of the CE.

Different Na compositions of the rhombohedral-NaSiCON were studied by varying the Na content from $\text{Na}_4\text{Zr}_2\text{Si}_3\text{O}_{12}$ to $\text{Na}_1\text{Zr}_2\text{P}_3\text{O}_{12}$. To keep charge neutrality in $\text{Na}_4\text{Zr}_2\text{Si}_3\text{O}_{12}$ upon the “removal” of Na^+ ions (i.e., addition of vacancies), the Si^{4+} ions must also be substituted by P^{5+} ions. Hence, we used the so-called “coupled” CE model⁵⁷ that constraints the concentration of $\text{Si}^{4+}/\text{P}^{5+}$ to Na^+/Va by utilizing a

single “point” term (ζ_i) of Eq. 1. The point term in a CE typically sets μ and the presence of a single μ ensures charge neutrality of the underlying NaSiCON within the CE. Given the large number of clusters available versus the number of DFT-calculated configurations, we used the compressive sensing approach to determine the absolute values of the ECIs by employing $\alpha = 1.5 \times 10^{-5}$ to penalize the L1-norm of the ECIs and minimize overfitting.⁵⁸

Different Na/Va and Si/P configurations were enumerated using the pymatgen package.⁵⁹ The primitive cell of the experimental rhombohedral $\text{Na}_4\text{Zr}_2\text{Si}_3\text{O}_{12}$ structure⁶⁰ (2 f.u., with 42 atoms) was used to enumerate the configurations in the possible Na concentration range ($0 \leq x \leq 3$) at a step-size, $\Delta x = 0.5$. To keep the number of possible configurations to a computationally tractable level, we used an electrostatic ranking scheme based on the Ewald energy,⁶¹ where classical point charges are assigned to each species ($\text{Na} = +1$, $\text{Zr} = +4$, $\text{Si} = +4$, $\text{P} = +5$, and $\text{O} = -2$). We selected 500 symmetrically distinct structures at each x with the lowest Ewald energies. Additionally, we applied a similar enumeration and ranking procedure to obtain Na/Va and Si/P configurations in $2 \times 1 \times 1$ supercells (4 f.u., with 84 atoms, equivalent to $1 \times 2 \times 1$ and $1 \times 1 \times 2$) of the primitive cell with a step-size, $\Delta x = 0.25$. In total, we computed 1192 structurally distinct orderings using DFT as implemented in VASP.^{62,63}

The exchange-correlation energy in DFT was approximated by the strongly constrained and appropriately normed (SCAN) semi-local meta-generalized gradient approximation (GGA) functional.⁶⁴ The accuracy of SCAN has been demonstrated on oxides and phosphates,^{65–67} where SCAN has been shown not to overbind O_2 gas, as is typical in GGA functionals.⁶⁸ Wavefunctions were expanded in terms of a plane-wave basis set, truncated at a kinetic energy cut-off of 520 eV and combined with projector augmented-wave (PAW) potentials to describe the core electrons.⁶⁹ The PAW potentials used were Na_pv 19Sep2006 $2p^6 3s^1$, Zr_sv 04Jan2005 $4s^2 4p^6 4d^2 5s^2$, Si 05Jan2001 $3s^2 3p^2$, P 06Sep2000 $3s^2 3p^3$ and O 08Apr2002 $2s^2 2p^4$. Total energies were integrated on a

$3 \times 3 \times 3$ Monkhorst-Pack grid⁷⁰ for the primitive cells (while the k -point density was maintained for the larger supercells), and converged within 10^{-5} eV/cell, without preserving any symmetry. The atomic forces (and stresses) were converged to within 10^{-2} eV/Å (0.29 GPa).

3 Results

3.1 The Energetics of the Na and Si/P Configurations in the Rhombohedral-NaSiCON

The formation energy (E_f) of each ordering, computed by DFT, is defined with respect to the lowest energy end-member compositions, $\text{Na}_4\text{Zr}_2\text{Si}_3\text{O}_{12}$ and $\text{Na}_1\text{Zr}_2\text{P}_3\text{O}_{12}$, using Eq. 2

$$E_f = E[\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}] - \frac{x}{3}E[\text{Na}_4\text{Zr}_2\text{Si}_3\text{O}_{12}] - \left(1 - \frac{x}{3}\right)E[\text{Na}_1\text{Zr}_2\text{P}_3\text{O}_{12}]. \quad (2)$$

where $E[\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}]$, $E[\text{Na}_4\text{Zr}_2\text{Si}_3\text{O}_{12}]$ and $E[\text{Na}_1\text{Zr}_2\text{P}_3\text{O}_{12}]$ are the DFT total energies of each Na/Va + Si/P ordering, and the two end-members. Figure 2 plots the formation energy vs. Na composition, which is the phase diagram of the rhombohedral-NaSiCON system at 0 K. The DFT formation energies are shown in yellow whereas the formation energies predicted by the CE model are shown in blue (Figure 2a). The convex envelopes of the structures with the lowest formation energies –the convex hull– as predicted by DFT and CE are depicted by solid yellow and solid blue lines, respectively. Importantly, the three lowest energy (or ground state) configurations that lie on both the DFT and CE hulls occur at Na compositions of $x = 0.0$, 2.0 , and 3.0 , in agreement with experimental observations.^{29,71} Thus, there should be a distinct, stable Na/Va (and Si/P) ordering corresponding to the $x = 2.0$ ground state configuration, apart from the $x = 0.0$ and $x = 3.0$ end-members.

Note that the ground state at $\text{Na}_3\text{Zr}_2\text{Si}_2\text{P}_1\text{O}_{12}$ ($x = 2.0$) distorts away from rhombohedral symmetry upon DFT structure relaxation, which indicates the tendency for the rhombohedral-NaSiCON to transform

into the stable low-temperature monoclinic NaSiCON.^{29,37,72,73} In Figure 2a, most orderings in $2 \times 1 \times 1$ supercells exhibit higher formation energies than configurations within the primitive cell. For example, all the configurations that exhibit $E_f < -50$ meV/f.u. at $x = 0.5$, 1.0 , 1.5 , 2.0 and 2.5 are orderings within the primitive cell.

3.2 The Cluster Expansion Model

Of the 1192 distinct orderings computed by DFT (Figure 2a), only 884 configurations were selected to fit the CE model Hamiltonian. The reduction of our data set is due to the high (and expected) mobility of Na ions in specific starting configurations, which causes Na ions to move from their initial positions during the structure relaxation to final positions that are symmetrically equivalent to other initial Na configurations. We removed selected high energy structures, primarily at $x = 0$ and 0.25 , that undergo appreciable distortion upon geometry relaxation with DFT. The ECIs obtained via fitting the CE to the DFT formation energies are depicted in Figure 3.

The ECIs of Figure 3 are obtained by minimizing the root mean square error (RMSE) against the DFT energies of all 884 configurations, which is ~ 11.20 meV/f.u. (~ 0.53 meV/atom), while minimizing the total magnitude of all ECIs to minimize overfitting.⁵⁸ The transferability of the CE is assessed via the leave one-out cross-validation (LOOCV) score, which is ~ 24.9 meV/f.u. (1.18 meV/atom). The 65 clusters with non-zero ECIs are listed in Table S2 of the SI.

Of the 65 ECIs, 38 ECIs are pair interactions, 22 are triplets and 4 are quadruplets. In Figure 3, a negative ECI indicates “attractive” interactions between Va for clusters built on Na/Va sites and P for clusters consisting of Si/P sites. Since the NaSiCON structure has both Na/Va and Si/P sites, attractive interactions are also extended to other species with the same occupational variable. Specifically, our CE model uses an identical notation for the occupation of Na/Si ($\sigma = 0$) and Va/P ($\sigma = +1$). Thus, a negative ECI on a

Figure 2: Formation energy of the rhombohedral-NaSICON vs. Na/Va (x) and Si/P ($3-x$) composition (panel a). Yellow dots are the formation energies from DFT, while blue crosses depict the energies from the cluster expansion model. The DFT and CE convex hulls are shown by solid yellow and blue lines. Panel b plots the error of the CE model with respect to DFT (horizontal axis) vs. the energy above the convex hull (vertical axis). The dashed lines in b are confidence windows (of ± 10 and ± 20 meV/f.u.) for the CE model.

Na/Va-Si/P pair translates to an attractive interaction that favors the occupation of Va (on the Na/Va site) and P (on the Si/P site). Similarly, positive ECIs indicate “repulsive” interactions between Va and P. Due to the specific assignment of $\sigma = 0$ for any Na/Si occupation, only clusters that are fully constituted by Va and/or by P contribute to non-zero ECIs towards the overall energy estimation in our CE model. The dominant pair and triplet terms in Figure 3, i.e., highest absolute magnitude ECI, are the repulsive pair cluster #34 (Na/Va-Na/Va of length ~ 7.40 Å), the attractive pair cluster #65 (Na/Va-Na/Va, ~ 9.19 Å), and the triplet cluster #92 (Na/Va-Na/Va-Na/Va, ~ 4.72 Å), respectively. All dominant pair, triplet and quadruplet interactions within our CE model are listed in Tables S3, S4 and S5 of the SI.

Remarkably, our CE model captures some important physics of the system. For example, the attractive pair #6 (in Figure S1 of the SI) fa-

vors Va located within the cluster formed by one Na(1) and one Na(2) site, separated by a length ~ 3.162 Å within the primitive rhombohedral cell. However, a larger (~ 6.52 Å) pair cluster #27 (in Figure S1 of the SI) with Na(1) and Na(2) sites is repulsive, which favors either a Na-Va or a Na-Na occupation within the pair. Thus, the interplay between pair #6 and #27 indicates the competition between short-range vs. long-range ordering phenomena in the structure. Furthermore, the most dominant triplet is ECI #92, is repulsive, penalizes the Va-Va-Va occupation and consists of one Na(1) and two Na(2) sites within the primitive cell (size < 4.73 Å), see Table S1 in SI. Hence, ECI #92 captures the rather strong short-range interaction between symmetrically distinct Na sites, i.e., Na(1) and Na(2) (as elucidated in Section 3.5). Also, the triplet ECI #92 likely acts in conjunction with pairs #27 and #6 (both involving Na(1) and Na(2) sites) to favour a Va-Na-Na configuration on the Na(1)-Na(2)-

Figure 3: Plot of the 65 ECI values (in meV/multiplicity, vertical axis) of each cluster vs. their size (in Å, horizontal axis). Negative (positive) ECIs in pairs are attractive (repulsive) interactions between Va-Va, P-P, and Va-P. The indexes of specific ECIs are indicated (Table S2 in SI).

Na(2) sites, which is the underlying motif of the ground state at $x = 2$ at 0 K (see Figure 2a and Section 3.5). Finally, the quadruplet ECIs #113 and #118 are attractive, span across Na/Va and Si/P sites, and favour occupations of Va-Va-Va-P and Va-Va-P-P, respectively, which likely indicate the electrostatic attraction between Va and P species.

The error in formation energies predicted by the CE expansion model are compared with the energy above the convex hull in Figure 2b, with two regions of confidences, ± 10 and ± 20 eV/f.u. (dashed lines). Importantly, the CE reproduces well the DFT formation energies within ~ 100 meV/f.u. above the convex hull line. In Figure 2b, points near 0 meV/f.u. on the horizontal axis represent a perfect fit with the DFT data, whereas points beyond ± 20 meV/f.u. can be considered poorly described by the model. Most of the formation energies predicted by the CE model lie within the ± 20 meV/f.u. window, which indicates that the CE can also reproduce

the formation energies of several high energy configurations accurately.

3.3 Temperature-Composition Phase Diagram of the Rhombohedral $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$

Using large simulation cells (172,032 atoms) with GCMC, we can coarse-grain⁷⁴ the grand-canonical potential at any Na(Va)/Si(P) concentration and temperature. The temperature vs. Na-composition phase diagram, as obtained via GCMC simulations, is shown in Figure 4. The phase boundaries of Figure 4 are identified by analyzing the grand-canonical potential energies, the discontinuities of Na concentration (vs. μ), and the variation of the heat capacity (vs. μ). Numerical hysteresis arising from the GCMC was removed by performing a free-energy integration (see Section S4 and Figure S2 of the SI).⁷⁴ A representative snapshot of GCMC simulations is provided in Figure S3.

Figure 4: Predicted composition (horizontal axis) vs. temperature (vertical axis) phase diagram of rhombohedral- $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ from GCMC simulations. Red stars indicates diffraction studies of rhombohedral-NaSiCON reported experimentally.^{33,40,60,75–79}

The phase diagram in Figure 4 contains four single-phase (or monophasic) regions, which are labelled as A (yellow), B (green) C (dark purple) and C' (light purple), with three two-phase (or biphasic) regions separating the monophasic domains. The biphasic regions are A+B (red dome between $0 < x < 2$, $T < 650$ K), A+C' (orange dome, $T > 650$ K), and B+C (blue dome between $2 < x < 3$). The monophasic regions can be described as, A: Na-poor domain, similar to the rhombohedral- $\text{Na}_1\text{Zr}_2\text{P}_3\text{O}_{12}$; C: Na-rich domain, similar to $\text{Na}_4\text{Zr}_2\text{Si}_3\text{O}_{12}$; B: high-conductivity domain based on the $\text{Na}_3\text{Zr}_2\text{Si}_2\text{P}_1\text{O}_{12}$ configuration, which is the target composition in experimental studies; and C': a high-temperature disordered domain that encompasses both $\text{Na}_3\text{Zr}_2\text{Si}_2\text{P}_1\text{O}_{12}$ and $\text{Na}_4\text{Zr}_2\text{Si}_3\text{O}_{12}$ regions. Experimentally the Na/Va and Si/P lattices in rhombohedral-NaSiCON are known to disorder in the composition range $1 < x < 3$ (i.e., excluding the end members) and at high temperatures (> 473 K),^{9,32,33,33,72,80} in qualitative agreement with our predicted phase diagram.

In the case of the B-phase (green domain in Figure 4), at temperatures < 150 K, phase B is only stable at near $x = 2$, but its stable composition range increases progressively with increasing temperature to a maximum range of $1.25 \leq x \leq 2.5$ at 650 K. The region of stability of the B-phase also overlaps with the composition ($1.8 \leq x \leq 2.2$) and temperature (< 415 K) where the rhombohedral structure transforms into the monoclinic polymorph in experiments.^{29,30,72} Thus, the presence of the B-phase may facilitate the rhombohedral-to-monoclinic transition. At temperatures above 650 K, a high-temperature disordered phase C' appears, which encompasses both the B and C monophasic regions. The miscibility gap that separates the B and C monophasic regions (blue dome in Figure 4), reaches its critical point at $x = 2.5$ and 650 K. The transition from the high-temperature disordered C' phase to the miscibility gap (i.e., the B+C two phase region) represents a first-order phase transition, and marked by the dashed black line at 650 K.

The experimental compositions, which are assigned to single-phase regions and deter-

mined from X-ray and neutron diffraction measurements, are shown as red stars in Figure 4.^{40,60,72,75-79} Most experimentally observed compositions are found in the single phase regions of A, B, C or C', and in good agreement with our calculated phase diagram. Exceptions are reported single-phase structures at $x = 2$ – 2.3 at 443 K, $x = 0.1$ and 2.35 at 300 K,³³ and $x = 1$ at 473 K.⁴⁰ Although most of the disagreements with experimentally reported single-phase compositions lie at (or near) the predicted phase boundaries, the measured, low temperature data point at $x = 2.35$, 300 K significantly deviates from our predictions. Notably, the experimental literature, so far, on $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ has never reported any phase separation in this system.

3.4 Na/Vacancies and Si/P Configurational Effects on the Structural Properties

The DFT-calculated volumes (panel a) and lattice constants a and c (panel b) of the various configurations as a function of the Na composition are shown in Figure 5. Stars represent experimentally reported values of volumes, lattice constants and c/a ratio,^{29,32,33,60,75-80} while dots, squares and triangles are the DFT-predicted values. The color of each point in Figure 5 is associated with its energy above the convex hull (Figure 2a), with darker blue (lighter white) indicating structures that are near (far away from) the convex hull. The black-dashed lines connect volumes, lattice constants and c/a ratio of structures forming the convex hull.^{29,32,33,43,81}

Moving from $x = 0$ to $x = 2$ in Figure 5a, the predicted volume increases monotonically with a maximum at $x = 2$ ($\text{Na}_3\text{Zr}_2\text{Si}_2\text{P}_1\text{O}_{12}$), in excellent agreement with experimental reports (distribution of stars). Although DFT calculations do not capture the effect of temperature, the agreement between theory and experiments on lattice volumes can be attributed to the low thermal expansion ($< 5\%$, $11.8 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) with increasing temperature (over a wide temperature range, i.e., $25 < T < 700 \text{ }^\circ\text{C}$) of

Figure 5: DFT-calculated volumes (vertical axis) in panel a and lattice constants a and c in panel b of rhombohedral NaSiCON vs. composition x (horizontal axis). In panel c the c/a ratio is shown. Each dot, square or triangle is colored according to its energy above the convex hull. Dashed black line connects ground state configurations that are on the convex hull at 0 K. Experimentally reported volumes and lattice constants^{29,32,33,60,75–80} at specific concentrations are indicated by stars.

NaSiCON.^{60,75} In the case of lattice parameters (Figure 5b), we observe that the a parameter increases monotonically with increasing Na content, while the c parameter increases for $0 < x < 2$ and decreases for $x > 2$, in excellent agreement with experimental studies.^{29,33} As the Na content increases in $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ in the range $0 < x < 2$, the Na^+ are displaced from Na(1) into Na(2) sites (Figure 6d, e and f). The reduced occupation of Na(1) sites facilitates the electrostatic repulsion between ZrO_6 units stacked along the c direction, resulting in an increase in the c parameter.

Importantly, we predict a mild volume contraction ($\sim 1\%$, panel a) for $x > 2$, in agreement with experimental observations that $\text{Na}_4\text{Zr}_2\text{Si}_3\text{O}_{12}$ has a lower volume than $\text{Na}_3\text{Zr}_2\text{Si}_2\text{P}_1\text{O}_{12}$ ($\sim 1\%$ smaller) due to a contraction of the c axis (panel b).⁷⁵ The reduction of the c/a ratio with increasing Na concentration (Figure 5c) captures the typical behavior of the rhombohedral-NaSiCON as the Na content is varied (stars in panel c).

3.5 Thermodynamic Properties and Na occupations vs. Temperature

The GCMC data enable the analysis of relevant thermodynamic properties, e.g., the Gibbs energy (G , orange dots and lines) and the configurational entropy (S , green dots and lines) functions. These are shown in Figure 6, for 3 distinct temperatures, **a** 445 K, **b** 625 K, and **c** 905 K centered around the B+C $\rightarrow$ C' transition (~ 650 K). Note that the Gibbs energies are referenced to the ground state end-member configurations, namely $\text{Na}_1\text{Zr}_2\text{P}_3\text{O}_{12}$ and $\text{Na}_4\text{Zr}_2\text{Si}_3\text{O}_{12}$. Panels d-f in Figure 6 show the extent of occupation of Na(1) (blue dots and lines) and Na(2) (red dots and lines) by Na^+ vs. x at three temperatures, where a fully Na-occupied site (fully empty) has an occupancy of 1.0 (0.0). Notably, the occupation values are obtained as statistical averages from GCMC simulations. Also, the multiplicity of Na(2) is three times that of Na(1), i.e., there are three Na(2) sites for every Na(1). Dashed lines in

all panels of Figure 6 indicate thermodynamic properties and Na occupancies within biphasic regions.

An increasing temperature typically decreases G , which is consistent with the more negative Gibbs energies at 905 K compared to 445 K in Figure 6. While S depends strongly on the temperature, the value of S at a given x depends on the number of accessible configurations at that composition. For example, $S(x = 3) = 0$ at all temperatures since there are no configurational degrees of freedom available at the $\text{Na}_4\text{Zr}_2\text{Si}_3\text{O}_{12}$ composition, i.e., no configurations lie above the convex hull at this composition (Figure 2).

Below the $\text{B}+\text{C}\rightarrow\text{C}'$ transition (445 and 625 K), $S(x)$ shows three distinct segments for the three monophasic regions A, B and C, with three minima of $S(x)$ (and $G(x)$) located at the 0 K ground state compositions, namely, $x = 0$, 2, and 3. The higher entropy observed for other compositions away from the 0 K ground states is indicative of the higher configurational disorder within the Na/Va and Si/P sub-lattices. Importantly, the minima in entropy at $x \sim 2$ (within the B monophasic region) at 625 K and 445 K correlates with the Na occupancies of the Na(1) and Na(2) sites (Figures 6d-f, see discussion below). At 905 K (beyond the $\text{B}+\text{C}\rightarrow\text{C}'$ transition), $S(x)$ shows two distinct segments, corresponding to the A and C' monophasic region.

Unraveling the distribution of Na among the Na(1) and Na(2) sites can shed light on the Na-ion transport in NaSiCON phases, which is still not fully understood.³⁷ From Figures 6d-f, we note that for $x = 0$, Na(1) is fully occupied and Na(2) is empty at all temperatures, in agreement with previous reports indicating that $\text{Na}_1\text{Zr}_2\text{P}_3\text{O}_{12}$ is a fully ordered phase, with Na occupying only Na(1).^{71,75} Similarly, at $x = 3$, both Na(1) and Na(2) sites are fully occupied, in agreement with the observations of Hong et al.²⁹ Interestingly, within the monophasic A region ($x = 0$ to $x \sim 1$) at 905 K, the occupation of Na(2) increases with increasing x , while Na(1) remains fully occupied (Figure 6f). At higher sodium contents, i.e., $x > 2$ (within C'), the occupation of Na(1) increases monotonically to-

wards 1.0 at $x = 3$, while the occupation of Na(2) remains roughly constant (~ 1.0). However, at intermediate Na contents ($x \sim 1.25$ to $x \sim 1.75$), the occupancies of Na(2) and Na(1) show contrasting trends with increasing Na content, i.e., as Na(2) sites are occupied by Na, Na(1) sites become unoccupied. This simultaneous occupation and un-occupation of Na(2) and Na(1) sites results in a decrease of configurational entropy (Figure 6c), which eventually reaches a minima at $x \sim 1.75$.

Similar trends in Na(1) and Na(2) occupancies at intermediate Na concentrations can also be observed below the $\text{B}+\text{C}\rightarrow\text{C}'$ transition (panels d and e in Figure 6), in agreement with the trends reported by Boilot and Collin (starts in panels d and e).³³ Notably, the Na(1) sites become empty at Na compositions of $1.5 < x < 2$ within the B domain (at 445 K and 625 K), whereas the Na(1) site is never fully empty in C' with the minimum in occupation reaching at $x \sim 1.75$. Also, the Na sites are completely ordered, i.e., Na(2) is fully occupied and Na(1) is fully empty, at $x = 2$ within the B-phase, whereas complete ordering does not occur at $x = 2$ within the high-temperature C' phase, underlying the key difference between the B and C' monophasic regions. Thus, Na occupying the Na(1) sites is the primary mechanism of inducing configurational disorder in the NaSiCON structure as the system transitions from ordered B to disordered C', particularly at $x = 2$. Additionally, the complete ordering at $x = 2$ in B corresponds to the minima in entropy observed at 445 K and 625 K at $x = 2$ (Figure 6a-b).

4 Discussion

4.1 Reconciling the Phase Behavior in NaSiCON-based Electrolytes and Electrodes

Understanding the thermodynamic properties of the rhombohedral- $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$, and NaSiCON systems in general, is of importance for the development of inexpensive solid electrolytes and electrode materi-

Figure 6: Thermodynamic properties (left panels, a, b and c) and Na occupancy (right panels, d, e, and f) are shown as a function of Na composition (x , horizontal axis). Gibbs free energy $G(x)$ (orange, left vertical axis) and configurational entropy $S(x)$ (in green, right vertical axis) are shown at specific temperatures 445 K (panel a), 625 K (panel b) and 905 K (panel c), respectively. Similarly, panels d, e, and f display the distribution of Na between the two sites, Na(1) (in blue) and Na(2) (in red), at 445 K, 625 K and 905 K, respectively. Experimental data at 443 K and 623 K from Ref. 33 are indicated as blue/red stars for Na(1)/Na(2) sites. Dashed lines indicate regions of phase separation in the phase diagram, while monophasic domains are shown by colored regions (from Figure 4).

als for novel Na-ion batteries. We have systematically analyzed the phase-diagram of rhombohedral- $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ by combining first-principles calculations, the cluster expansion formalism, and Monte Carlo simulations. The computed phase diagram of Figure 4 reveals the presence of two main regions characterized by biphasic behavior, which are: i) the A+B region that stretches through Na compositions $0 < x < 2$ at low temperatures (below 200 K) and narrows in composition range with increasing temperature, ii) the miscibility gap, B+C, in the region $2 < x < 3$ between 0 and

~ 650 K. Our result is in stark contrast with experimental literature, which indicates a single phase behavior across the whole region of accessible Na compositions (i.e., $0 \leq x \leq 3$) and temperatures (> 450 K, beyond the region of monoclinic phase stability).^{9,30,32,33,39,40,72} The phase diagram also displays four monophasic regions —A, B, C and C', with B spanning a noticeably increasing range of Na concentrations with increasing temperature. Note that Zr off-stoichiometry is often observed in the rhombohedral- $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$, with residual ZrO_2 found after high-temperature syn-

thesis and sintering treatments.^{9,31,39,40,82} Our computed phase diagram does not account for Zr off-stoichiometry, and the inclusion of an additional compositional axis would make this study intractable in terms of computational complexity. However, Boilot et al.³² confirmed that Na migration in vacant Zr sites is impeded, indicating that Zr deficiency is less relevant for optimizing the Na-conductivity of this material.

Few experimental reports have targeted the structural characterization of rhombohedral- $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ at Na compositions $0 < x < 2$ or $2 < x < 3$.^{29,40} Notably, most of the early characterization work on rhombohedral $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ used single crystal samples with $x \geq 2$,^{30,33,72,83,84} which were mostly refined according to the structural model of Hong.²⁹ While single-crystal X-ray diffraction (XRD) experiments are undoubtedly useful in understanding the structural properties of this material, they may hinder the observation of phase separation in $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$, in particular, across Na-rich and Na-poor composition domains (e.g., A+B and B+C in Figure 4), resulting in the lack of identification of unique mono or biphasic domains. For this purpose, advanced powder X-ray or neutron diffraction experiments are required since they should identify phase separation and reveal all the crystalline phases that would eventually co-exist in a given sample.

Recent bench³¹ and synchrotron⁴⁰ powder XRD studies demonstrated unequivocally that the low temperature $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ compositions behave as a single phase, in contrast to our predictions. For example, Deng et al.⁴⁰ reported a single phase at $\text{Na}_2\text{Zr}_2\text{Si}_1\text{P}_2\text{O}_{12}$ at temperatures of 295 and 473 K, which is in the middle of the A+B two-phase region (Figure 4). The disagreement in terms of phase stabilities at low temperatures (< 500 K) between the theory-predicted thermodynamics (suggesting phase-separation) and experimental reports (indicating single-phase behavior) can be also attributed to kinetic factors. For example, at low temperatures (~ 300 K), our predicted phase diagram suggests that $\text{Na}_{3.5}\text{Zr}_2\text{Si}_1\text{P}_2\text{O}_{12}(\text{C}')$ will phase separate into a mixture of $\text{Na}_3\text{Zr}_2\text{Si}_2\text{P}_1\text{O}_{12}$ (B) and

$\text{Na}_4\text{Zr}_2\text{Si}_3\text{O}_{12}$ (C). This requires the disordered SiO_4^{4-} and PO_4^{3-} ions in the high temperature C' phase to be redistributed in order to form the stable B and C phases. The redistribution of the SiO_4^{4-} and PO_4^{3-} , which requires macroscopic diffusion of multivalent Si^{4+} and P^{5+} ions, would involve high activation barriers that are inaccessible at the lower temperatures to ensure full phase separation.⁸⁵ However, it remains to be verified experimentally (which we will do in the near future) whether prolonged annealing treatments at intermediate temperatures can promote phase separation in $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$.

Biphasic behavior is typical in NaSiCON-based electrodes. For example, Delmas et al.⁴² detected phase separation of the rhombohedral electrode $\text{Na}_2\text{Ti}_2(\text{PO}_4)_3$ when cooled, leading to the formation of $\text{Na}_3\text{Ti}_2(\text{PO}_4)_3$ and $\text{Na}_1\text{Ti}_2(\text{PO}_4)_3$. For NaSiCON-electrodes with a single transition metal (e.g., M = Ti, V, Cr and Fe in $\text{Na}_x\text{M}_2(\text{PO}_4)_3$), the existence of two-phase domains is also observed in electrochemical experiments, whereby the Na-discharge voltage profile exhibits a flat plateau as Na intercalates in the electrode (see Figure 7).^{42,47} Notably, mechanisms of phase separation in single-transition-metal NaSiCON-electrodes do not involve modifications of the structural framework since phase separation occurs across Na compositions (i.e., the formation of Na-rich and Na-poor domain) and bond breaking/reforming involving framework atoms (e.g., Ti, V, Cr or Fe) is not required, as transition metals do not have to diffuse macroscopically. In other words, the mobile Na^+ and the accompanying electrons can be redistributed swiftly even at low temperatures (~ 300 K) to ensure phase separation. Interestingly, previous studies have claimed that the thermodynamically favorable phase-separation was curbed in mixed transition-metal NaSiCON systems. For example, in $\text{Na}_2\text{ZrCr}(\text{PO}_4)_3$ the phase separation reaction, $2\text{Na}_2\text{ZrCr}(\text{PO}_4)_3 \rightarrow \text{NaZr}_2(\text{PO}_4)_3 + \text{Na}_3\text{Cr}_2(\text{PO}_4)_3$, is inhibited by the slow kinetics of bond-breaking/reforming Zr–O and Cr–O bonds and the poor macroscopic diffusivity of Zr^{4+} and Cr^{3+} .⁴² Notably, phase separation of $\text{Na}_2\text{ZrCr}(\text{PO}_4)_3$ was not observed

even after prolonged annealing treatments at high temperatures. Thus, the thermodynamically favored phase separation in rhombohedral- $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ may also be kinetically inhibited, similar to the mixed transition-metal NaSiCON systems.⁴⁴

To illustrate explicitly the similarity between the phase-separation behavior identified in this work in $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ and as observed in NaSiCON electrodes, we schematically superimpose our computed phase diagram (around 295 K) onto the experimental voltage charge/discharge curves of the $\text{Na}_3\text{Ti}_2(\text{PO}_4)_3$, $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, $\text{Na}_3\text{Cr}_2(\text{PO}_4)_3$ and $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ in Figure 7.

Figure 7 shows that as Na is inserted/extracted into/from $\text{NaM}_2(\text{PO}_4)_3/\text{Na}_3\text{M}_2(\text{PO}_4)_3$ ($\text{M} = \text{Ti}, \text{V}, \text{Cr}$ and Fe), the materials always phase separate for Na concentrations in the range $0 < x < 2$. $\text{Na}_{x+1}\text{V}_2(\text{PO}_4)_3$ also phase separates between Na concentrations of $2 < x < 3$. Importantly, Figure 7 identifies that at composition $x = 2$ a stable phase (or structure/configuration) is always found and appears to be common to all NaSiCON-based electrodes, analogous to $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$. Intriguingly, at low temperature and at $x = 2$ all of the Na(2) sites in $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ are occupied while the Na(1) sites have negligible occupations, similar to trends observed in Figure 6.^{29,33,80} On the basis of our entropy curves of Figure 6, we believe that the tendency for Na to order at composition $x = 2$ in $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, $\text{Na}_3\text{Cr}_2(\text{PO}_4)_3$ and $\text{Na}_3\text{Zr}_2\text{Si}_2\text{P}_1\text{O}_{12}$ is significant, and eventually drives the rhombohedral to monoclinic (and their superstructures) phase transition at room temperature.^{29,73,86}

In light of these findings one can formulate the following hypothesis:

- Phase separation appears to be the underlying favorable thermodynamic process in $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$, but is inhibited by the large energy barrier involved in the rearrangement of the SiO_4^{4-} and PO_4^{3-} species.
- Phase separation is fully or partially inhibited, kinetically, whenever cations of the $\text{M}_2(\text{PO}_4)_3$ framework are required

to break bonds, migrate and form new bonds. Analogous to the kinetic impediment to phase separation observed for the solid electrolyte $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$, partial replacement of SiO_4^{4-} and PO_4^{3-} may also kinetically limit any phase separation in mono-transition metal electrodes. Other “network formers”, such as SiS_4^{4-} and PS_4^{3-} found in Li-ion conductors may provide similar effects.⁸⁷

- In both the solid electrolyte and NaSiCON-electrodes, the existence of a stable ordering of Na-ions on the Na(2) site at the $x = 2$ composition is a common feature. The stability of the fully occupied Na(2)+fully empty Na(1) configuration might be electrostatically driven (see Section 4.2) and requires further exploration. As is well established in the literature, at low temperatures, this peculiar Na configuration seems to promote the phase transition from rhombohedral into monoclinic symmetry, with the rhombohedral→monoclinic transformation mechanism needing more work to understand fully.

The validation of these hypotheses and their extension to all NaSiCON-derived electrodes requires further experimental and computational investigations.

4.2 Na Distributions and Effects on Na Transport in $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$

The bulk ionic conductivity of $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ is set by the occupations of Na(1) and Na(2) sites,^{31,33,35,37} which enables Na^+ percolation along Na(1)–Na(2)–Na(1) paths. While Zhang et al.³⁷ investigated the existence of a 3rd Na site, Na(3), located between Na(1) and Na(2); Na(3) is negligibly occupied at high temperatures $200 < T < 800^\circ\text{C}$, hence not relevant to the thermodynamics. Occupancies of Na(1) and Na(2) sites are in turn determined by the distribution of SiO_4^{4-} and PO_4^{3-} groups, in order to maintain “local” charge-neutrality within the

Figure 7: Experimental voltage (vertical axis) charge/discharge curves of $\text{Na}_3\text{Ti}_2(\text{PO}_4)_3$ (in red), $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (in green), $\text{Na}_3\text{Cr}_2(\text{PO}_4)_3$ (in blue), and $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ (in yellow), adapted from Refs. 43,45,47,81, are superimposed onto the predicted phase diagram of NaSiCON (~ 295 K) from Figure 4. The dashed line and the arrow indicate the ordering at $x = 2$.

rhombohedral- $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$, an aspect that has been rarely discussed in prior experimental reports. Furthermore, the higher mobility of Na enables Na^+ ions to adopt energy minimizing configurations, given a Si/P arrangement. Thus, the interplay of local charge neutrality, the short and long-range cluster interactions among the Na(1) and Na(2) sites, and Na^+ mobility will control the experimentally observed population of Na sites at different Na concentrations.

The GCMC data show that the occupation of the Na(1) site decreases from $x = 0$ to $x = 2$, and increases monotonically between $x = 2$ and $x = 3$ below the $\text{B}+\text{C} \rightarrow \text{C}'$ transition (see Figure 6). For site Na(2), we observe a constant increase of its occupation in the range $0 < x < 2$, while Na(2) remains fully occupied for $x > 2$. The trends in occupancies of Na(1) and Na(2) sites are in excellent agreement with the experimental study of Boilot et al.³³ Importantly, the highest Na-conductivity observed in the rhombohedral structure is at $x \sim 2$, which coincides with the high degree of occupation of Na(2) sites and the largely empty Na(1) sites. The selective occupation of Na(2) sites at $x \sim 2$ can be attributed to the shorter distance between

Na(2) sites and XO_4 tetrahedra, where the increasing occupation of Si in the XO_4 units with increasing x can electrostatically favor Na occupation of Na(2) sites. However, it remains to be seen how specific configurations of Na/Va and Si/P affect the microscopic migration barriers that govern the overall Na-transport. Hence, it is important to extend our model by incorporating migration barriers, as a function of Na content and temperature, which will be the focus of future work.

5 Conclusion

In this work, we investigated the phase stability of the high-temperature $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ ionic conductor using a multi-scale approach based on first-principles calculations, a cluster expansion framework, and large-size Monte Carlo simulations. We observed excellent agreement with DFT predicted structural properties, namely lattice volumes, c and a parameters, with measurements. Additionally, we found that the selective occupation of Na(2) sites instead of Na(1) sites drives the stability of the $\text{Na}_3\text{Zr}_2\text{Si}_2\text{P}_1\text{O}_{12}$ ground state, particularly

at low temperatures. The computed phase diagram suggests that $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ would phase separate into three distinct single-phase domains at low temperature, in contrast with experimental observations so far. Kinetic limitations, specifically the macroscopic diffusion of Si^{4+} and P^{5+} ions, may inhibit the phase separation into Na+Si-rich and Va+P-rich domains in experiments. We identified similarities in phase behavior between the NaSiCON-electrolyte and mono-transition-metal NaSiCON electrodes, which typically phase separate upon Na extraction/insertion. Interestingly, the lack of phase separation observed in mixed-transition-metal NaSiCON electrodes may be attributed to kinetic limitations, similar to the scenario in $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$. Therefore, we speculate that the introduction of SiO_4^{4-} into phosphate-based electrodes can inhibit kinetically phenomena of phase separation. Based on our phase diagram, we also unveil the complex interplay by Na sites occupation at different temperatures and electrostatic. With this understanding, we could identify and explain why experimentally only specific compositions offers high Na-transport. Finally, our work offers important insights on the role of Na-Va and Si-P configurations on the stability and Na-transport properties of NaSiCON-electrolytes and will be an important addition in the development of safe and sustainable Na-ion batteries.

Author Contribution

P.C. designed supervised every aspect of the project. Z. D. and P. C. performed the DFT calculations and fitted the cluster expansion model. Z. D. Modified the CASM code, performed the Monte Carlo calculations and carried out the data analysis. Z. D. and P. C. wrote the first draft. Z. D., P. C., G. S. G. and A. K. C. contributed to the initial data analysis of the computed data. All the authors contributed to the discussion and the final version of this manuscript.

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Supporting Information Available

The Supporting Information contains: i) the detail of the CE model, ii) a detailed description of the Monte Carlo simulation, iii) the identification of the phase boundaries, and iv) a discussion on the free-energy integration. All the computational data associated with this study are freely available at the repository <https://github.com/caneparesearch/NaZrSiPO-paper-data>.

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Phase Behavior in NaSiCON

Electrolytes and Electrodes

—Supplementary Information—

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S1 Model Structure of $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$

Table S1 shows the atom labels and coordinates of the model-structure cell of $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ on which the cluster expansion is fitted.

Table S1: Atom labels and fractional coordinates of the model-structure cell of $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ in the rhombohedral representation. Space group $R\bar{3}c$ No. 167, lattice constants $a = 9.099 \text{ \AA}$ and $\alpha = 60.634^\circ$ as obtained from Ref. 1, ICSD # 15546, with stoichiometry $\text{Na}_4\text{Zr}_2\text{Si}_3\text{O}_{12}$. The types of Na, i.e. Na(1) and Na(2) in reference to Figure 1 in the main article are also indicated.

Atomic species	Label site	x	y	z
Na/Va	0 Na(1)	0.500000	0.500000	0.500000
Na/Va	1 Na(1)	0.000000	0.000000	0.000000
Na/Va	2 Na(2)	0.889670	0.610330	0.250000
Na/Va	3 Na(2)	0.610330	0.250000	0.889670
Na/Va	4 Na(2)	0.250000	0.889670	0.610330
Na/Va	5 Na(2)	0.389670	0.750000	0.110330
Na/Va	6 Na(2)	0.750000	0.110330	0.389670
Na/Va	7 Na(2)	0.110330	0.389670	0.750000
Zr	8	0.352810	0.352810	0.352810
Zr	9	0.852810	0.852810	0.852810
Zr	10	0.647190	0.647190	0.647190
Zr	11	0.147190	0.147190	0.147190
Si/P	12	0.545440	0.954560	0.250000
Si/P	13	0.954560	0.250000	0.545440
Si/P	14	0.250000	0.545440	0.954560
Si/P	15	0.045440	0.750000	0.454560
Si/P	16	0.750000	0.454560	0.045440
Si/P	17	0.454560	0.045440	0.750000
O	18	0.432310	0.228140	0.579990
O	19	0.228140	0.579990	0.432310
O	20	0.579990	0.432310	0.228140
O	21	0.932310	0.079990	0.728140
O	22	0.079990	0.728140	0.932310
O	23	0.728140	0.932310	0.079990
O	24	0.567690	0.771860	0.420010
O	25	0.771860	0.420010	0.567690
O	26	0.420010	0.567690	0.771860
O	27	0.067690	0.920010	0.271860
O	28	0.920010	0.271860	0.067690
O	29	0.271860	0.067690	0.920010
O	30	0.469130	0.125870	0.329030
O	31	0.125870	0.329030	0.469130
O	32	0.329030	0.469130	0.125870
O	33	0.969130	0.829030	0.625870
O	34	0.829030	0.625870	0.969130
O	35	0.625870	0.969130	0.829030
O	36	0.530870	0.874130	0.670970
O	37	0.874130	0.670970	0.530870
O	38	0.670970	0.530870	0.874130
O	39	0.030870	0.170970	0.374130
O	40	0.170970	0.374130	0.030870
O	41	0.374130	0.030870	0.170970

S2 Analysis of the Effective Cluster Interactions

Table S2 and Figure S1 report the characteristics of the 65 distinct effective cluster interactions (ECIs) of the $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ system in our cluster expansion (CE) model. Figure S1 plots the most significant ECIs (normalised by their multiplicity) as function of their index #.

Table S2: ECIs. Point term $\mathcal{PT}$, pair $\mathcal{P}$, triplet $\mathcal{T}$, and quadruplet $\mathcal{Q}$ terms. Site refer to the label sites given in Table S1. Cell $[0, 0, 0]$ is the reference cell. M is the multiplicity of each cluster.

Index	Cluster Index	Type	Site(Label)	Cell	Min. (Å)	Max. (Å)	ECI (meV)	ECI/M (meV)
1	4	$\mathcal{PT}$	Na/Va(3)	$[0, 0, 0]$	—	—	+54.194	+27.097
2	5	$\mathcal{P}$	Na/Va(3) Si/P(14)	$[0, 0, 0]$ $[0, 0, 0]$	3.055	3.055	−399.759	−33.313
3	6	$\mathcal{P}$	Na/Va(0) Na/Va(3)	$[0, 0, 0]$ $[0, 0, 0]$	3.162	3.162	−435.435	−72.572
4	8	$\mathcal{P}$	Na/Va(3) Si/P(17)	$[0, 0, 0]$ $[0, 0, 0]$	3.710	3.710	−570.255	−47.521
5	12	$\mathcal{P}$	Na/Va(3) Na/Va(6)	$[0, 0, 0]$ $[0, 0, 0]$	4.727	4.727	−42.419	−3.535
6	13	$\mathcal{P}$	Si/P(14) Si/P(15)	$[0, 0, 0]$ $[0, -1, 1]$	4.922	4.922	+141.637	+11.803
7	14	$\mathcal{P}$	Na/Va(3) Na/Va(5)	$[0, 0, 0]$ $[0, 1, -1]$	4.980	4.980	+58.296	+9.716
8	15	$\mathcal{P}$	Na/Va(3) Na/Va(4)	$[0, 0, 0]$ $[1, -1, 0]$	5.102	5.102	+1193.520	+99.460
9	19	$\mathcal{P}$	Na/Va(3) Si/P(15)	$[0, 0, 1]$ $[1, -1, 0]$	6.056	6.056	−385.829	−32.152
10	20	$\mathcal{P}$	Si/P(14) Na/Va(0)	$[0, 0, 0]$ $[0, 0, 1]$	6.173	6.173	+46.582	+3.882
11	21	$\mathcal{P}$	Na/Va(3) Si/P(14)	$[0, 0, 0]$ $[1, -1, 0]$	6.196	6.196	−17.857	−1.488
12	22	$\mathcal{P}$	Na/Va(3) Si/P(17)	$[0, 0, 0]$ $[0, 1, 0]$	6.220	6.220	−352.738	−29.395
13	24	$\mathcal{P}$	Na/Va(3) Na/Va(0)	$[0, 0, 0]$ $[0, 0, 1]$	6.465	6.465	+468.440	+39.037
14	27	$\mathcal{P}$	Na/Va(3) Na/Va(0)	$[0, 0, 0]$ $[0, -1, 1]$	6.519	6.519	+913.329	+76.111
15	30	$\mathcal{P}$	Na/Va(3) Si/P(15)	$[0, 0, 0]$ $[0, -1, 1]$	6.901	6.901	+339.229	+28.269
16	31	$\mathcal{P}$	Na/Va(3)	$[0, 0, 0]$	6.956	6.956	+11.663	+1.944

			Na/Va(5)	[0, 0, 0]				
17	32	$\mathcal{P}$	Si/P(14) Si/P(15)	[0, 0, 0] [1, 0, 0]	7.012	7.012	+3.121	+0.260
18	33	$\mathcal{P}$	Na/Va(3) Na/Va(7)	[0, 0, 0] [1, -1, 0]	7.263	7.263	-61.571	-5.131
19	34	$\mathcal{P}$	Na/Va(3) Na/Va(4)	[0, 0, 0] [0, -1, 0]	7.406	7.406	+670.671	+111.779
20	36	$\mathcal{P}$	Si/P(14) Si/P(16)	[0, 0, 0] [0, 0, 0]	7.478	7.478	-145.242	-24.207
21	38	$\mathcal{P}$	Na/Va(3) Si/P(12)	[0, 0, 0] [0, -1, 0]	7.857	7.857	-445.839	-37.153
22	42	$\mathcal{P}$	Na/Va(3) Si/P(13)	[0, 0, 0] [-1, 1, 0]	8.083	8.083	+276.618	+23.051
23	44	$\mathcal{P}$	Na/Va(3) Si/P(14)	[0, 0, 0] [0, -1, 0]	8.198	8.198	-377.133	-31.428
24	46	$\mathcal{P}$	Na/Va(3) Na/Va(5)	[0, 0, 0] [1, -1, 0]	8.483	8.483	+15.930	+2.655
25	49	$\mathcal{P}$	Si/P(14) Na/Va(0)	[0, 0, 0] [-1, 1, 0]	8.570	8.570	-23.865	-1.989
26	50	$\mathcal{P}$	Si/P(14) Si/P(15)	[0, 0, 0] [1, -1, 0]	8.608	8.608	+130.803	+10.900
27	52	$\mathcal{P}$	Na/Va(3) Na/Va(7)	[0, 0, 0] [1, 0, -1]	8.736	8.736	-46.095	-3.841
28	53	$\mathcal{P}$	Na/Va(3) Na/Va(2)	[0, 0, 0] [0, -1, 0]	8.856	8.856	+11.860	+1.977
29	62	$\mathcal{P}$	Na/Va(3) Na/Va(3)	[0, 0, 0] [1, 0, -1]	9.186	9.186	-68.224	-11.371
30	63	$\mathcal{P}$	Na/Va(3) Na/Va(3)	[0, 0, 0] [1, 0, -1]	9.186	9.186	-142.789	-11.899
31	64	$\mathcal{P}$	Si/P(14) Si/P(14)	[0, 0, 0] [0, 1, -1]	9.186	9.186	-215.821	-17.985
33	65	$\mathcal{P}$	Na/Va(0) Na/Va(0)	[0, 0, 0] [1, 0, -1]	9.186	9.186	-561.834	-93.639
33	66	$\mathcal{P}$	Si/P(14) Si/P(14)	[0, 0, 0] [0, 1, -1]	9.186	9.186	-21.014	-3.502
34	69	$\mathcal{P}$	Na/Va(3) Si/P(14)	[0, 0, 0] [0, 0, -1]	9.309	9.309	+165.373	+13.781
35	71	$\mathcal{P}$	Si/P(14) Si/P(16)	[0, 0, 0] [-1, 1, 0]	9.510	9.510	-142.597	-23.766
36	73	$\mathcal{P}$	Na/Va(3)	[0, 0, 0]	9.633	9.633	+21.698	+1.808

			Si/P(13)	$[0, -1, 0]$				
37	79	$\mathcal{P}$	Na/Va(3)	$[0, 0, 0]$	9.838	9.838	+419.493	+34.958
			Si/P(17)	$[-1, 0, 1]$				
38	82	$\mathcal{P}$	Na/Va(3)	$[0, 0, 0]$	9.879	9.879	+183.989	+15.332
			Si/P(12)	$[-1, -1, 1]$				
Index	Cluster Index	Type	Site(Label)	Cell	Min. ($\text{\AA}$)	Max. ($\text{\AA}$)	ECI (meV)	ECI/M (meV)
39	84	$\mathcal{T}$	Na/Va(3)	$[0, 0, 0]$				
			Na/Va(0)	$[0, 0, 0]$	3.056	3.739	-632.141	-52.678
			Si/P(14)	$[0, 0, 0]$				
40	85	$\mathcal{T}$	Na/Va(3)	$[0, 0, 0]$				
			Na/Va(0)	$[0, 0, 0]$	3.162	3.739	-343.491	-28.624
			Si/P(13)	$[0, 0, 0]$				
41	86	$\mathcal{T}$	Na/Va(3)	$[0, 0, 0]$				
			Na/Va(0)	$[0, 0, 0]$	3.478	3.739	+112.125	+9.344
			Si/P(17)	$[0, 0, 0]$				
42	87	$\mathcal{T}$	Na/Va(3)	$[0, 0, 0]$				
			Si/P(14)	$[0, 0, 0]$	3.056	4.626	-8.603	-0.717
			Si/P(16)	$[0, 0, 1]$				
43	88	$\mathcal{T}$	Na/Va(3)	$[0, 0, 0]$				
			Si/P(14)	$[0, 0, 0]$	3.056	4.700	+147.373	+24.562
			Si/P(12)	$[0, -1, 1]$				
44	89	$\mathcal{T}$	Si/P(14)	$[0, 0, 0]$				
			Si/P(12)	$[0, -1, 1]$	4.700	4.700	+36.538	+18.269
			Si/P(13)	$[-1, 0, 1]$				
45	91	$\mathcal{T}$	Na/Va(3)	$[0, 0, 0]$				
			Na/Va(6)	$[0, 0, 0]$	3.162	4.727	+210.952	+17.579
			Si/P(13)	$[0, 0, 0]$				
46	92	$\mathcal{T}$	Na/Va(3)	$[0, 0, 0]$				
			Na/Va(0)	$[0, 0, 0]$	3.477	4.727	+2969.345	+247.445
			Na/Va(6)	$[0, 0, 0]$				
47	93	$\mathcal{T}$	Na/Va(3)	$[0, 0, 0]$				
			Si/P(14)	$[0, 0, 0]$	3.056	4.922	+124.056	+10.338
			Si/P(17)	$[0, 0, 0]$				
48	96	$\mathcal{T}$	Si/P(14)	$[0, 0, 0]$				
			Si/P(15)	$[0, 0, 0]$	4.626	4.922	+101.874	+8.490
			Si/P(16)	$[-1, 0, 1]$				
49	98	$\mathcal{T}$	Na/Va(3)	$[0, 0, 0]$				
			Na/Va(4)	$[1, -1, 0]$	3.055	5.102	-167.327	-13.944
			Si/P(13)	$[0, 0, 0]$				
50	99	$\mathcal{T}$	Na/Va(3)	$[0, 0, 0]$	3.4779	5.102	-483.709	-40.309

			Na/Va(4)	[1, -1, 0]				
			Na/Va(1)	[1, 0, 1]				
51	100	$\mathcal{T}$	Na/Va(3)	[0, 0, 0]	4.727	5.102	+85.713	+7.143
			Na/Va(4)	[1, -1, 0]				
			Na/Va(7)	[1, 0, 0]				
52	101	$\mathcal{T}$	Na/Va(0)	[0, 0, 0]	4.727	5.102	-193.556	-16.130
			Na/Va(4)	[1, -1, 0]				
			Na/Va(6)	[0, 0, 0]				
53	102	$\mathcal{T}$	Na/Va(3)	[0, 0, 0]	5.1025	5.1025	-96.748	-24.187
			Na/Va(4)	[1, -1, 0]				
			Na/Va(2)	[0, -1, 1]				
54	104	$\mathcal{T}$	Si/P(14)	[0, 0, 0]	3.739	5.629	+913.076	+76.090
			Na/Va(0)	[0, 0, 0]				
			Si/P(12)	[0, 0, 0]				
55	105	$\mathcal{T}$	Si/P(14)	[0, 0, 0]	4.626	5.629	+183.298	+15.275
			Si/P(12)	[0, 0, 0]				
			Si/P(17)	[0, 0, 0]				
56	107	$\mathcal{T}$	Si/P(14)	[0, 0, 0]	4.922	5.629	-64.742	-5.395
			Si/P(12)	[0, 0, 0]				
			Si/P(15)	[0, 0, 0]				
57	108	$\mathcal{T}$	Si/P(14)	[0, 0, 0]	5.623	5.623	-110.756	-27.689
			Si/P(12)	[0, 0, 0]				
			Si/P(13)	[0, 0, 0]				
58	109	$\mathcal{T}$	Na/Va(3)	[0, 0, 0]	3.056	5.733	-15.573	-2.595
			Si/P(14)	[0, 0, 0]				
			Na/Va(2)	[-1, 0, 1]				
59	110	$\mathcal{T}$	Na/Va(3)	[0, 0, 0]	4.727	5.733	-237.045	-19.754
			Na/Va(6)	[0, 0, 0]				
			Na/Va(5)	[0, -1, 1]				
60	111	$\mathcal{T}$	Na/Va(3)	[0, 0, 0]	5.103	5.733	-54.373	-9.062
			Na/Va(4)	[1, -1, 0]				
			Na/Va(2)	[0, 0, 0]				
61	112	$\mathcal{T}$	Na/Va(3)	[0, 0, 0]	5.733	5.733	-32.485	-16.243
			Na/Va(4)	[0, -1, 1]				
			Na/Va(2)	[-1, 0, 1]				
Index	Cluster Index	Type	Site(Label)	Cell	Min. (Å)	Max. (Å)	ECI (meV)	ECI/M (meV)
62	113	$\mathcal{Q}$	Na/Va(3)	[0, 0, 0]	3.162	4.727	-648.492	-54.041
			Na/Va(0)	[0, 0, 0]				
			Na/Va(6)	[0, 0, 0]				
			Si/P(17)	[0, 0, 0]				

63	115	$\mathcal{Q}$	Na/Va(3)	[0, 0, 0]	3.056	4.922	-125.232	-10.436
			Na/Va(6)	[0, 0, 0]				
			Si/P(13)	[0, 0, 0]				
			Si/P(17)	[0, 0, 0]				
64	118	$\mathcal{Q}$	Na/Va(3)	[0, 0, 0]	3.162	4.922	-748.192	-62.349
			Na/Va(0)	[0, 0, 0]				
			Si/P(13)	[0, 0, 0]				
			Si/P(17)	[0, 0, 0]				
65	119	$\mathcal{Q}$	Na/Va(3)	[0, 0, 0]	3.056	4.981	-55.110	-9.185
			Si/P(14)	[0, 0, 0]				
			Na/Va(5)	[0, 0, 1]				
			Si/P(16)	[0, 0, 1]

Figure S1: Relevant ECIs as function vs. their cluster index as fully detailed in Table S2. The point term is not shown.

S3 Basis of the Cluster Expansion and ECI assignation

An occupational basis was utilised and thus σ is assigned $\text{Na} = 0$, $\text{Va} = 1$, and $\text{Si} = 0$, $\text{P} = 1$. Therefore only clusters which are occupied by Va (on Na/Va sites) and/or P (on Si/P sites) in a given structure contribute non-zero ECIs to the overall CE model. The sign of the ECIs identify whether the interactions are attractive (negative ECIs) or repulsive (positive ECIs) between Va, P and across Va and P. While an attractive ECI favors all sites in a given cluster to be occupied by Va and/or by P, a repulsive ECI favors the occupation of at least one of the sites in the cluster by Na or Si. Tables S3, S4, and S5 lists the most prominent, in terms of magnitude, attractive and repulsive pair, triplet, and quadruplet ECIs, respectively.

Table S3: Unique ECI pairs (in meV) normalised by their multiplicity.

ECI #	Species	ECI
Attractive		
5	Va-P	-33.313
6	Va-Va	-72.572
8	Va-P	-47.521
19	Va-P	-32.152
22	Va-P	-29.395
36	P-P	-24.207
38	Va-P	-37.153
44	Va-P	-31.428
64	P-P	-17.985
65	Va-Va	-93.639
71	Va-P	-23.766
Repulsive		
15	Va-Va	+99.460
24	Va-Va	+39.037
27	Va-Va	+76.111
30	Va-P	+28.269
34	Va-Va	+111.779
42	Va-P	+23.051
79	Va-P	+34.958

Table S4: Unique ECI triplets (in meV) normalised by their multiplicity.

ECI #	Species	ECI
Attractive		
84	Va-Va-P	-52.678
85	Va-Va-P	-28.624
99	Va-Va-Va	-40.309
102	Va-Va-Va	-24.187
Repulsive		
92	Va-Va-Va	+247.445
104	P-Va-P	+76.090

Table S5: Unique ECI quadruplets (in meV) normalised by their multiplicity.

ECI #	Species	ECI/M (meV)
Attractive		
113	Va-Va-Va-P	-54.041
118	Va-Va-P-P	-62.349

S4 Thermodynamic Integration

As shown in Figure S2, the grand-canonical Monte Carlo (MC) scans were performed in the chemical potential (μ) and temperature (T) space. The scan started at $T = 5$ K and up to 1605 K with a step $\Delta T = 5$ K at $\mu = -1, 0$ and 1 eV/f.u. Then at every T , μ was scanned in both forward ($\mu = -1.0$ to 1.0 eV/f.u.) and backward ($\mu = 1.0$ to -1.0 eV/f.u.) directions with a step size of $\Delta\mu = 0.005$ eV/f.u. as shown in Figure S2. In general, μ was scanned across 2 concentration ranges, namely, between $x = 0$ and 2 ($\mu = -1.0$ to 0.0 eV/f.u.), and $x = 2$ and 3 ($\mu = 0.0$ to 1.0 eV/f.u.), due to the existence of the 3 ground-state structures on the convex hull ($x = 0, 2$ and 3 , see manuscript).

The phase boundary was found at the intersections of the grand-canonical potential energy Φ^α for each phase α (A, B and C) as defined in Figure S2. Φ is defined by Eq. 1

$$\Phi = [E - TS] - \mu c \quad (1)$$

In panel

Figure S2: **a** Schematic showing how the phase boundary (dashed lines) was identified in the (μ, T) space. The arrows show both the MC scan and the thermodynamic integration directions. At phase boundaries, potential surfaces $\Phi^\alpha(\mu, T)$ on the both sides intersects with each other. The phase boundaries in the (x, T) space are then converted from the compositions at the phase boundary in (μ, T) space. **b** An example (at $T = 105$ K) of the grand potential (Φ) depending on chemical potential (μ, T), along with the strategy to choose the phase boundaries (pink circles) is shown. **c** Variation of composition x and normalized heat capacity C_v vs. μ , at $T = 445$ K, as obtained from the Monte Carlo simulations is displayed. Discontinuities in the chemical potential μ represent phase transitions at specific concentrations x and are indicated by dashed lines in black.

where E is the total energy predicted by the cluster expansion model, S is the configurational entropy and c is the parametric composition. The parametric composition c in $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ is defined as in Eq. 2.

$$c = 1 - \frac{x}{3} \text{ with } 0 \leq c \leq 1. \quad (2)$$

For Monte Carlo scans at fixed μ and variable T , Φ is calculated using the thermodynamic integration in Eq. 3.

$$\Phi(\beta, \mu) = \frac{\beta_0}{\beta} \Phi_0(\beta_0, \mu) + \frac{1}{\beta} \int_{\beta_0}^{\beta} [E - \mu c] d\beta \quad (3)$$

$$\text{with } \Phi_0(\beta_0, \mu) = E - \mu c \quad (4)$$

where $\beta = 1/(k_B T)$ and k_B is the Boltzmann constant.

In Monte Carlo scans at variable μ and fixed T , Φ is defined in Eq. 5.

$$\Phi(\beta, \mu) = \Phi_0(\beta, \mu_0) - \frac{1}{\beta} \int_{\mu_0}^{\mu} c d\mu \quad (5)$$

$$\text{with } \Phi_0(\beta, \mu_0) = \Phi_{\text{heating}}(\beta, \mu_0) \quad (6)$$

Since the entropy effects are negligible at low temperatures (e.g., $T = 5$ K), the starting values of Φ_0 in T scans at 5 K are taken as $\Phi_0 = E - \mu c$. The thermodynamic integration at each μ starts from the $\Phi_{\text{heating}}(T, \mu_0)$ where $\mu_0 = -1, 0$ and 1 eV/f.u., and is scanned both forward and backward in the Region I and Region II as shown in Figure S2a. One of the examples is shown in Figure S2b.

After the thermodynamic integration, the phase boundary is identified by the intersection of grand-canonical potential envelopes in the (μ, T) space (dashed lines in Figure S2a) which is then converted into the (x, T) space. When the intersections is not well defined by the numerical data, discontinuities in c vs. μ and C_v vs. μ curves (see Figure S2c) are considered and the phase boundaries identified.

S5 Example of Monte Carlo Snapshot

Figure S3 shows a snapshot from the Monte Carlo simulations and three ground state structures at $x = 0, 2$ and 3 in $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ (right panel).

Figure S3: In the left panel, a portion of a snapshot of a Monte Carlo simulation ($x = 2$, $T = 445$ K), where a primitive cell of $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ is marked by the black hexagon (Na at both Na(1) and Na(2) sites are coloured silver). The primitive cells of the three ground state structures at $x = 0, 2$ and 3 for $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ are shown on the right.

References

- (1) Qui, D.; Capponi, J.; Joubert, J.; Shannon, R. Crystal structure and ionic conductivity in $\text{Na}_4\text{Zr}_2\text{Si}_3\text{O}_{12}$. *J. Solid State Chem.* **1981**, *39*, 219–229.