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DFT investigation of Na⁺ diffusion on a giant NaSiCON supercell

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Highlights

DFT investigation of Na⁺ diffusion on a giant Na_{1+x}Zr₂Si_xP_{3-x}O₁₂ ($0 \leq x \leq 3$) NaSICON supercell

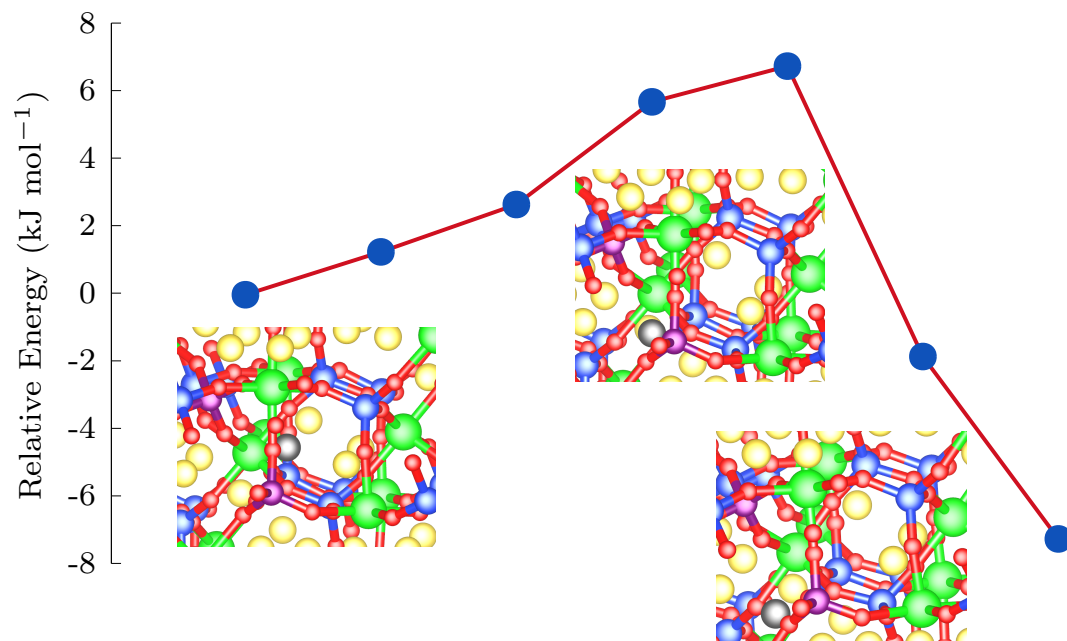
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- Energy barriers for sodium diffusion were calculated as a function of local environment
- Zirconium vacancies heavily inhibit diffusion in the investigated NaSICON
- The used supercell size should minimize spurious effects in periodic calculations

Graphical Abstract

DFT investigation of Na^+ diffusion on a giant NaSICON supercell

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DFT investigation of Na⁺ diffusion on a giant NaSICON supercell

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ABSTRACT

NaSICON is referred to a family of crystalline structures with the common property of an easy migration of sodium ions inside the crystal channels, a peculiarity that allows these materials to be employed in solid-state cells as electrolytes or even electrodes. Here we report the results of the investigation of the sodium migration process by means of density functional theory calculations on models of the non-stoichiometric NaSICON material $\text{Na}_{3.31}\text{Zr}_{1.67}(\text{SiO}_4)_{1.84}(\text{PO}_4)_{1.16}$. The size of the supercell used in this work should soften the spurious effects of periodicity on the final results, *i.e.* the activation energies corresponding to the migration of the Na⁺ ion between two topologically distinct sodium sites. Different local environments were investigated to highlight the dependence both on type and presence of atomic nuclei in the channel, thus obtaining the activation barriers of the migration process in the presence of single or multiple local Si/P substitutions, and in the presence of a Zr⁴⁺ ion vacancy. Concurrently, a structural analysis of the NaSICON cavities mainly involved in the process was carried out. The results obtained shed light on the effects of the alterations of the NaSICON local composition on the Na⁺ migration that, other than having an intrinsic interest per se, can be used as a starting point for statistical simulations.

1. Introduction

Nowadays, the term NaSICON (sodium super ionic conductor) is employed to indicate a whole series of structures with the general formula $\text{A}_x\text{MM}'(\text{XO}_4)_3$, where A = (Li, Na, K, Mg, Ca), M and M' = (Fe, V, Ti, Zr, Sc, Mn, Nb, In) and X = (S, P, Si, As). From a crystallographic point of view, NaSICON can be seen as consisting of octahedral units MO_6 and $\text{M}'\text{O}_6$, each connected with 3 XO_4 tetrahedral units. The amount of alkali or alkaline-earth ions, A, depends on the oxidation state of M and M', as well as on the nature of the non-metal units, X. These materials mostly find employment in electrochemical cells.

When used as electrodes, potentially components of sodium-ion batteries, [1, 2, 3, 4] the properties of NaSICON-type structures can be modulated by appropriately choosing the transition metals and/or the polyanionic groups. [5] Historically, the most important NaSICON families for this use were those containing vanadium [6, 7] and those containing titanium, [8, 9] but recently an incredible variety of them have been proposed such as those object of the study, based on the density functional theory, conducted by Zhang *et al.*: [10] $\text{Na}_4\text{Co}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$, $\text{Na}_2\text{Fe}_2(\text{SO}_4)_3$, $\text{Na}_3(\text{VO})_2(\text{PO}_4)_2\text{F}$, $\text{Na}_2\text{CoP}_2\text{O}_7$, $\text{Na}_3\text{MnZr}(\text{PO}_4)_3$, $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$, $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, $\text{Na}_2\text{MnP}_2\text{O}_7$, $\text{Na}_2\text{FePO}_4\text{F}$, $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$, $\text{NaFe}(\text{SO}_4)_2$, NaFePO_4 , $\text{Na}_3\text{MnTi}(\text{PO}_4)_3$. Among the most studied cathode materials there are also those with the general formula $\text{Na}_x\text{MM}'(\text{PO}_4)_3$, [11] indicated with the NVP acronym, and $\text{Na}_x\text{MM}'(\text{PO}_4)_2\text{F}_{3-2y}\text{O}_{2y}$ ($y = 0, 1$), [12] for which the NVPF acronym is employed, where $1 \leq x \leq 4$ and MM' can be one of the VV, VMn, MnTi, MnZr, VCr, VGa, VNi, VFe pairs. NVP and NVPF materials have a NaSICON-type structure giving them high multi-electronic capacity,

stability and a fast diffusion of sodium ions. Although in these systems there are four potentially removable Na⁺ ions, it is very difficult to obtain a reversible extraction/insertion cycle involving more than two Na⁺ ions. A step forward in this respect was recently made by Wang *et al.* [13] who in a particularly interesting investigation reported the computational prediction, synthesis and characterization of $\text{Na}_4\text{MnCr}(\text{PO}_4)_3$, showing a (de)intercalation of 2.35 sodium ions.

In the field of electrolytes, on the other hand, NaSICON materials find use in all-solid-state lithium ion, all-solid-state air, and hybrid batteries. Regarding, in detail, the diffusion of sodium ion in NaSICON, several computational studies have been performed using periodic approaches. In one of the first investigations, conducted by Bui *et al.* [14] and concerning the $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ structure, calculations showed that along the diffusion path preferred by sodium ions the highest energy barriers do not exceed 28 kJ mol⁻¹. Song *et al.* [15], instead, studied the $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ structure, estimating activation barriers for the diffusion of Na⁺ of the order of 10 kJ mol⁻¹ along two preferential directions. More recently Arjmandi *et al.* [16] studied the migration of all species present in structures of the type $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$; whereas Xu *et al.* [17] found a barrier of about 30 kJ mol⁻¹ for the diffusion of Na⁺ in $\text{Na}_4\text{VMn}_{0.5}\text{Fe}_{0.5}(\text{PO}_4)_3$ supported on carbon. Finally, Tian *et al.* [18] suggested, on the basis of computational results, that doping with Ca²⁺ ions may be useful to avoid the steric restrictions encountered in the migration paths of sodium, while Wu *et al.* [19] proposed to use structures containing the MoO_4^{2-} ion for this purpose.

In this work, we intend to examine, by means of calculations based on density functional theory (DFT), the diffusion process of the sodium ion in selected model structures mimicking the system with formula $\text{Na}_{3.31}\text{Zr}_{1.67}(\text{SiO}_4)_{1.84}(\text{PO}_4)_{1.16}$, which presents a large variety of different environments

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of the migration channel due to crystal defects. We will refer to these systems by using the general term NaSICON. The evaluation of the volume of the main cavities that characterize the sodium migration channel (experimentally due to the different synthesis conditions that cause different stoichiometries, substitutions, vacancies and doping), will be associated with a DFT study of the energetics of the diffusion processes of the Na⁺ ions. The aim is to identify the best chemical and structural conditions that favor the migration process of sodium ions; the data thus obtained have the dual purpose of: i) be able to serve as a guide in the production of increasingly high-performance NaSICON materials and ii) be used as a very accurate starting point for statistical simulations [20, 21] that link micro- and macroscopic aspects of this material. For instance, the investigation of Wang and coworkers [21] focused on the Na⁺ ion transport in NaSICON materials with formula Na_xM₂(PO₄)₃ (M = Ti, V, Cr; x = 1–4), joining energy data obtained from DFT with kinetic Monte Carlo simulations. The main conclusions are that the Na⁺ diffusion characteristics are heavily affected by the local chemical environment involved in the migration channel. It is clear that the reliability of interpretations and predictions of the local effects on the diffusive behavior of sodium relies heavily on the availability of accurate and robust data calculated on atomistic models.

As mentioned above, DFT is widely used for predicting new materials in this field, and it works quite accurately. Accuracy issues can, however, arise when characterizing solid-phase diffusion, particularly in the case of the materials under consideration, where activation energies for the process may be low and exhibit a high error bar, thus causing discrimination problems. It is true that new-generation DFT functionals achieve quite high accuracies, but in most cases they introduce computational complexity that inhibits their routine use for periodic systems; in fact, it is extremely common for periodic systems to use exchange-correlation functionals within the generalized gradient approximation. Therefore, if functionals that guarantee greater accuracy cannot be chosen, then models that allow for limiting spurious periodicity effects, primarily interactions between defects or substitutions and the inhibited local relaxation of the structure, should be employed. With this in mind, the calculations reported in this work were performed on a supercell which, to the best of our knowledge, is the largest ever used.

2. Computational Methods

In the present investigation, all calculations on the NaSICON system were performed at the DFT level using the PBE exchange-correlation functional, the software of choice being Quantum Espresso (QE) v7.3 [22, 23]. For the description of the core electrons, the Vanderbilt's scalar relativistic ultrasoft pseudopotentials [24] were employed. In accordance with this choice, in both calibration and production calculations the cutoff on charge density and potential was always set to be 10 times the one on plane wave functions. After several preliminary trials, we chose to use

the values of 50 Ry and 500 Ry for the wavefunction and density cutoff parameter, respectively, in all the subsequent production calculations. A further refinement in this cutoff values does not produce significant changes in the electronic energy associated with the NaSICON structure. In fact, these cutoff values are in agreement with those generally found in the literature for similar kind of systems.

The energy barriers involved in the migration process of sodium ions from one topological site to another were estimated using the QE implementation of the *climbing image nudged elastic band* (CI-NEB) method. Seven images (including the reactant and product geometries) were commonly employed for these calculations; the convergence threshold on the forces was set to 0.05 eV/Å.

NaSICON has an extremely dense structure, which is difficult to analyze and rationalize using traditional visualization software for crystalline structures. For this reason, it was decided to implement a small software that could facilitate the present study. It is called Cash (Crystal Analysis Shell) and, as the name suggests, it has a command line interface through which the user can manipulate and obtain information on the crystal structure under investigation. Cash is freely available under the MIT license, and its source code can be found on GitHub [25]. Its main features consist in the visualization of the surroundings of an atomic nucleus (or, more generally, of any point in space) through the selection of other nuclei of the crystal structure that are included in a spherical volume of radius defined by the user. This procedure generates a "ball", *i.e.* a small xyz file that contains a subset of the original crystal structure that can be examined with any molecular editor of choice. In this way, it is possible: i) to grasp in a more effective and immediate way the differences between various topological sites of the same element; ii) to visualize the distortions that a vacancy produces on the elements that should have coordinated the absent nucleus; iii) to have an ordered list of the closest nuclei (first, second, ... coordination sphere) to a given site.

Assuming that two balls have been generated by centering on two adjacent sodium nuclei, another interesting function of Cash is to merge these two files, so that any atoms present in both balls are listed only once. So, it is easy to obtain, for example, a detailed view of a migration channels. Finally, another function that has been useful for the analysis of the NaSICON structures considered in this study, is the calculation of the volume of a geometric solid whose vertex spatial coordinates are known. In this way it was possible to quantify the volume of the octahedral cavities defined by the oxygen nuclei around the sodium and zirconium sites, whether these nuclei are present or there are vacancies.

3. Results and Discussion

3.1. Choice of the model

The experimental structure for the system under investigation was taken from the crystallographic information file obtained from the diffractometric investigation by Rudolf et al. [26]. Accordingly, our specific NaSICON structure

crystallizes in the monoclinic lattice (C2/c space group), with crystallographic constants $(a,b,c) = (15.67, 9.07, 9.22)$ Å and $(\alpha, \beta, \gamma) = (90.0, 123.8, 90.0)^\circ$. This material, labeled SG-AM60, has formula $\text{Na}_{3.31}\text{Zr}_{1.67}(\text{SiO}_4)_{1.84}(\text{PO}_4)_{1.16}$ and is here considered representative of a non-stoichiometric NaSICON derived from hydrothermal synthesis, showing partial Si/P segregation, a relatively high percentage of Zr vacancies and a peculiar distribution of sodium ions inside the channels. SG-AM60 was chosen for the present study because its room-temperature monoclinic symmetry and high sodium-ion concentration would natively enable realistic diffusion modeling. Indeed, within atomistic *ab initio* frameworks, high mobile-ion density and fractional site occupancy inherently mimic the defective landscape required for efficient hopping characterization without introducing artificial defects. SG-AM60 could be therefore appropriate for investigating sodium transport in disordered, sol-gel or hydrothermally synthesized NaSICON materials by means of a number of simulation approaches, which would be the natural scope of use of the computational data reported in this work.

In the following the main structural characteristics of the model will be highlighted. Three different topological sites for the sodium ion are present, labeled as Na1, Na2 and Na3, which differ in their coordination surroundings and have site occupancy (i.e. the fraction of a specific crystallographic site filled by a particular atom or molecule) of 83%, 98% and 75%, respectively. It can be observed that the Na1 site has six sodium ions as its Na neighboring neighbors, and all of them of the Na2 and Na3 types; Na2 and Na3, in turn, have five sodium Na1 ions around them. Regarding the silicon and phosphorus nuclei, they share the same sites inside the cell. Since silicon is the predominant element, the presence of phosphorus in place of silicon was here considered as a substitution in a formal $\text{Na}_4\text{Zr}_2(\text{SiO}_4)_3$ unit. There are two different topological sites for the Si/P pair: in the first one the ratio between the two elements is 70:30, while in the second one it is 57:43. Finally, as regards zirconium nuclei, they are present in a single topological site inside the cell, whose percentage of occupation is 83.5%, thus indicating a discrete number of zirconium vacancies in the crystal lattice.

It is worth to note that the diffractometric investigation reports a crystalline structure resulting from an average of local environments that are present in the macroscopic crystal. This is not suitable for a computational study of an ultimately atomistic nature, in which the investigated systems cannot be macroscopic and for which it is necessary to use an exactly defined structure. The computational study, therefore, was performed by building models that allowed us to describe a well-contextualized local portion of this NaSICON structure, in which a certain Si/P ratio or the presence of a zirconium vacancy occur, within a larger structure that has a regular and properly defined stoichiometry. Since it is not possible to deal with fractional site occupations, for the initial structure used in DFT calculations we considered both the three sodium sites and the zirconium site occupied at 100%, and the sites related to the silicon-phosphorus pair occupied only

and exclusively by silicon. This pristine structure was taken as a reference to be used to compare the effects of the silicon-phosphorus substitutions, as well as the consequences of the zirconium vacancy.

With this in mind, a conventional translational asymmetric cell with stoichiometry $\text{Na}_{16}\text{Zr}_8(\text{SiO}_4)_{12}$ (twice as large as the primitive cell, see Figure 1a) was generated. This cell was then used for calibration calculations (i.e. convergence with respect to wave function cutoff) but not for production ones, essentially because its too small dimensions would have given rise to fictitious interactions between the substitution/vacancies present in the cell and those in its periodic images, thus describing a system having a much higher defect density than the one observed experimentally. These fictitious interactions would have the effect of: i) preventing a correct description of the distortions caused by vacancies and substitutions; and, consequently, ii) falsify the results related to the sodium migration process. The situation is further complicated by the fact that the activation barriers for the sodium diffusion process in NaSICON are expected of low magnitude. It was then decided to adopt for production a model system consisting of a supercell eight times larger than the conventional cell used for calibration (Figure 1b), which makes the present study unique in the computational literature on NaSICON, and presumably one of the most accurate from the point of view of the model employed. The supercell in question (hereafter referred to as SU) was constructed by replicating the conventional cell twice along each cell vector, thus obtaining a 672-atom structure with stoichiometry $\text{Na}_{128}\text{Zr}_{64}(\text{SiO}_4)_{96}$. We are confident that this allows for greater accuracy in the obtained structural and energetic results since the fictitious interactions between defects are minimized, at the cost of course of being able to employ a considerable computational power. As a matter of fact, in order to make the calculations possible on this 672-atom supercell, real plane waves were used to construct the electron density of the system (i.e., only the Γ point was considered), with the effect of greatly lighten the requirements in terms of resources for the calculations.

3.2. Optimized supercell

The QE variable cell optimization of SU returned a primitive monoclinic lattice having the following cell parameters: $a = 32.181$ Å, $b = 18.589$ Å, $c = 18.372$ Å, $\beta = 125.358^\circ$. Looking again at the different sodium topological sites in the optimized structure, it can be noted that Na2 and Na3 converge to the same site: as a matter of fact, one can be converted into the other by means of a reflection operation. The most obvious difference between the two sites as they appear in the experimental cif concerns the first coordination sphere of the sodium ions, since Na3 has more sodium ions close than Na2. By removing the crystal defects, i.e. in the absence of silicon-phosphorus substitutions and sodium and zirconium vacancies, it was obtained a degeneracy of the two Na2 and Na3 sites into what it seems to be a single topological center. For this reason, even considering the way in which the three original sites are connected one another, in

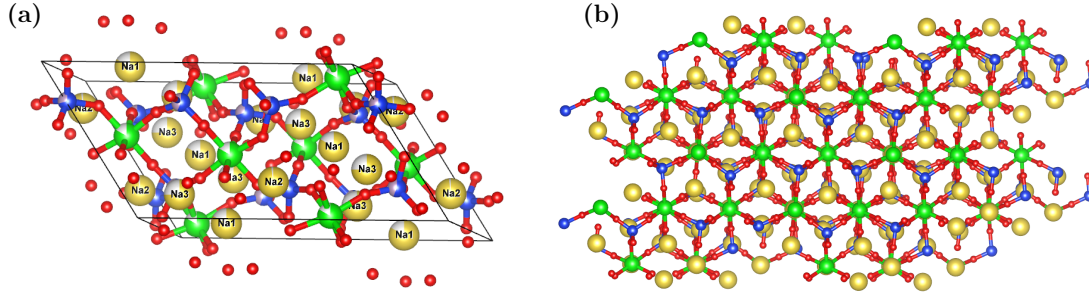


Figure 1: (a) Experimental structure as obtained from the crystallographic information file [26], from which the Na₁₆Zr₈(SiO₄)₁₂ cell used for the calibration studies was derived. The three types of occupied sites of the sodium ion are identified. The color code is Na: yellow, O: red, Zr: green, Si: blue, P: violet, vacancy: white. The two-color atomic centers reflect the occupancy of the corresponding sites. (b) The Na₁₂₈Zr₆₄(SiO₄)₉₆ supercell used in the production calculations.

order to study the sodium migration process the Na1 → Na2 and Na1 → Na3 channels were considered essentially equivalent. We will refer throughout indiscriminately to Na1 or Na2 both as a sites and as the sodium ion that possibly occupies it.

Figure 2(a) shows the migration channel between the Na1 and Na2 sites in SU, which were considered to study the diffusion of Na⁺ in the present NaSICON structure. Figures 2(b) and 2(c) report the oxygen coordination geometries around the sodium ions in the two sites, respectively. The coordination around Na1 can be described as an almost regular octahedron with an oblique rectangular base while the coordination around Na2 is a highly distorted octahedron with an oblique trapezoidal base. Figure 2(d) shows a detail of the aforementioned sodium migration channel, in which three different Si sites can be identified (where silicon ions can be potentially replaced by phosphorus ones), that show a different commitment in the coordination of the two sodium ions: σ_a coordinates Na2 with two oxygen atoms, one of which also coordinates Na1; σ_b coordinates Na2 with a single oxygen and Na1 with another one; σ_c coordinates Na1 and Na2 with the same oxygen atom. In addition to these three silicon atoms, a zirconium atom is present in the channel connecting the Na1 and Na2 sites, the absence of which, as we will see later, has a significant impact on the migration energetics.

3.3. Na⁺ migration with Si/P substitutions

In addition to computing the activation energy in the pristine condition given by the aforementioned supercell, all the combinations of Si⁴⁺/P⁵⁺ substitutions, as well as the Zr⁴⁺ vacancy, have been investigated to quantify the effect of different local environments on the sodium migration energetics. A nomenclature is now introduced that allows to quickly identify the specific supercell we are talking about by means of a string of the type “ $N_A:\sigma t$ ”, where N stands for NaSICON, $A \in \{+, -\}$ gives information about the presence or the vacancy, respectively, of the Zr nucleus in the Na2 → Na1 migration channel; $\sigma \in \{0, a, b, c, ab, ac, bc, abc\}$ indicates which Si⁴⁺ nuclei have

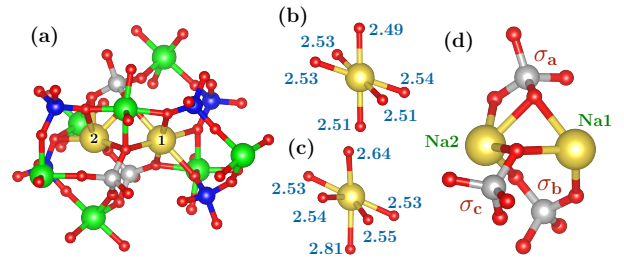


Figure 2: (a) Detail of the two cages around the Na1 and Na2 sites in the optimized geometry of SU; gray atomic centers are those involved in the Si/P substitution. For clarity, the other Na⁺ ions present in the moiety are not shown. (b, c) Coordination geometry around the sodium ion placed in the Na1 and Na2 site, respectively; the Na–O distances are in Å. (d) Detail of the migration channel, indicating the three types of sites (σ_a , σ_b , σ_c) with respect to which the Si/P substitution was considered.

been replaced with P⁵⁺ (e.g. 0 indicates no substitution at all, whereas ac indicates a substitution of both σ_a and σ_c silicon ions; see Figure 2 for sites definition); finally, $t \in \{none, 1, 2\}$ states whether the sodium vacancy is present and if it is in the Na1 or Na2 topological site, respectively. Accordingly, the only investigated systems without a sodium vacancy are $N_+ : 0$ and $N_- : 0$. The net charge of a system with Si/P replacements is equal to $n_\sigma + \delta_{Na}$, where $n_\sigma = 0, 1, 2, 3$ corresponds to the number of substitutions and $\delta_{Na} = 0, -1$ takes into account a Na⁺ vacancy, if present. Since we are only interested in energy differences between very similar structures and since the SU cell ensures good dilution of vacancies/substitutions [27, 28], only the mandatory neutralizing jellium background was included in the calculations, while we did not find it necessary to introduce post-processing corrections to deal with charged cells.

The above structures were handcrafted by submitting appropriately modified supercells to geometry optimization, so locating the minima in the potential energy surface related

to the initial and final points of the sodium migration process. To facilitate the rationalization of the results obtained, the geometric distortions that occur in these systems were summarized using a single parameter, namely the volume of the polyhedron (considered as a deformed octahedron) defined by the six oxygen atoms in the first coordination sphere around the (vacant or not) Na1 and Na2 sites, evaluated by means of the Cash utility. The obtained results were collected in Table 1. It is not surprising that the oxygen cage increases its volume (+12.0% for the Na1 site and +13.3% for the Na2 one) due to the introduction of a sodium vacancy; this has, however, a very limited effect (around 3%) for the other involved cage, *i.e.* the one from which Na⁺ diffuses. It can also be noted that the Si/P substitution has a slight effect on the volume of the coordination octahedrons. When the sodium vacancy is located in the Na1 site, the volume variation can reach up to +13.9% (*i.e.*, the case of $N_+:abc1$), showing an increase proportional to the number of substituted silicon atoms; where, at the same time, the increase in volume of the octahedral cavity around the occupied Na2 site is increasingly smaller. When, instead, Na2 is the vacant site, the behavior is more irregular, reflecting the strong deviation of this coordination site from a regular octahedron: the greater variety of Na–O interactions present in the Na2 site compared to the Na1 site (see Figures 2b and 2c) causes the variation of the cage volume to be significantly more dependent on the specific kind of Si/P substitution involved. Since, by construction, the oxygen cages that exist in $N_+:0$ represent the optimal situation for the coordination of the sodium ions, any distortion will presumably cause a decrease in the Na–O interaction energy. The explicit calculation allows to verify how important are the effects of the coordination variations on the diffusion energetics.

The results reported in Table 2 are related to the energy difference (ΔE_{21}) associated with the migration of the Na⁺ ion from a Na2 site to an adjacent Na1 site, as well as to the activation barriers corresponding to this process ($E_b^{\rightarrow}$) and to the reverse migration ($E_b^{\leftarrow}$). Given that effective diffusion should proceed between the Na1 and Na2 sites in an alternating manner, it is helpful to report also the kinetically resolved activation energy (E_b^{kr}), which, according to the definition of Van der Ven and Cerden [20], corresponds to the simple average of the energy barriers associated to the forward and backward processes. It is to note that, while our calculations focused on single-ion hops to establish baseline barriers for specific local chemical environments, concerted multi-ion diffusion may become significant at high sodium concentrations [21]; the single-hop data, however, should be sufficient to capture emergent cooperative behaviors when integrated into mesoscale statistical simulations.

The energy values collected in Table 2 can be interpreted by means of the following considerations. Focusing on the Si/P mono-substitutions, it can be noticed that the lowest activation value for the Na2→Na1 migration occurs in the system where P is in σ_a ($E_b = 3.4$ kJ mol⁻¹, *i.e.* essentially no barrier), while the highest one is found in the case of the σ_b substitution. The system having P in σ_c , on the other

Table 1

Volume of the octahedral cage surrounding the Na1 and Na2 sites in the optimized structures of the investigated NaSICON systems. The percentage change with respect to the volume of the corresponding cage in $N_+:0$ is reported in parentheses.

System	Volume/Å ³	
	Na1 site	Na2 site
$N_+:0$	17.829	16.150
$N_+:01$	19.875 (+12.0)	16.760 (+3.8)
$N_+:a1$	20.075 (+12.6)	16.649 (+3.1)
$N_+:b1$	19.985 (+12.1)	16.654 (+3.1)
$N_+:c1$	20.013 (+12.2)	16.685 (+3.3)
$N_+:ab1$	20.179 (+13.2)	16.308 (+1.0)
$N_+:ac1$	20.246 (+13.6)	16.337 (+1.2)
$N_+:bc1$	20.107 (+12.8)	16.304 (+1.0)
$N_+:abc1$	20.310 (+13.9)	15.997 (−0.9)
$N_+:02$	18.121 (+1.6)	18.300 (+13.3)
$N_+:a2$	18.175 (+1.9)	17.956 (+11.2)
$N_+:b2$	18.176 (+1.9)	18.246 (+13.0)
$N_+:c2$	18.165 (+1.9)	18.394 (+13.9)
$N_+:ab2$	18.245 (+2.3)	17.908 (+10.9)
$N_+:ac2$	18.294 (+2.6)	18.115 (+12.4)
$N_+:bc2$	18.214 (+2.2)	18.344 (+13.6)
$N_+:abc2$	18.361 (+3.0)	18.033 (+11.7)

hand, shows a smaller difference (1.1 kJ mol⁻¹) with respect to the 6.6 kJ mol⁻¹ calculated for the case of Na⁺ diffusion in the absence of Si/P substitutions. Furthermore, the ΔE_{21} data indicate that when Na⁺ diffuses in the system with P in σ_a there is a significant stabilization, while in the case of P in σ_b this is less pronounced (which helps keep the E_b^{kr} barrier within a reasonable value). For comparison, we note that the Boltzmann distribution at room temperature between two energy levels having an energy difference of just 6 kJ mol⁻¹ indicates a population ratio of about 12:1 in favor of the more stable level, while if the energy difference is halved the corresponding populations are in a ratio of about 3:1.

Table 2

Energy differences (ΔE_{21}), forward ($E_b^{\rightarrow}$), backward ($E_b^{\leftarrow}$) and kinetically resolved (E_b^{kr}) energies barriers calculated for the migration of a sodium ion from the Na2 to the Na1 site in the investigated NaSICON systems.

System	Energies/kJ mol ⁻¹			
	ΔE_{21}	$E_b^{\rightarrow}$	$E_b^{\leftarrow}$	E_b^{kr}
$N_+:01 \rightarrow N_+:02$	-3.6	6.6	10.2	8.4
$N_+:a1 \rightarrow N_+:a2$	-6.6	3.4	10.0	6.7
$N_+:b1 \rightarrow N_+:b2$	-3.1	9.6	12.7	11.2
$N_+:c1 \rightarrow N_+:c2$	-5.2	7.7	12.9	10.3
$N_+:ab1 \rightarrow N_+:ab2$	-7.2	6.8	14.0	10.4
$N_+:ac1 \rightarrow N_+:ac2$	-11.0	3.9	14.9	9.4
$N_+:bc1 \rightarrow N_+:bc2$	-4.7	12.8	17.5	15.2
$N_+:abc1 \rightarrow N_+:abc2$	-11.1	8.8	19.9	14.4

Comparison with the data obtained for those systems where two Si/P substitutions have occurred and where the effects of the substitutions of the various Si sites are strengthened or canceled out, allows us to outline that the substitution in the σ_a site makes easier the Na2→Na1 diffusion process, whereas the substitution in the σ_b site has a negative effect, and in the case of σ_c site the effect is negligible.

As a guideline for interpretation, it can be considered that the substitution of Si with P makes some of the coordinating oxygen atoms slightly depleted of electron density, which has negative impact on the Na–O interactions. Therefore, the behavior of the substituted systems can be explained by considering the different coordinating mode of the three σ_x ($x = a, b, c$ sites, see figure 2d): as a result of the Na2→Na1 migration when P is in σ_a , one PO–Na interaction is replaced by a SiO–Na interaction (favorable effect), while when P is in σ_c the same PO–Na interaction is found both in the reagent and in the product (neutral effect). Finally, to explain the properties of P in σ_b , we take into account that following diffusion the PO–Na interaction is replaced by another interaction of the same kind (the only difference being the oxygen atom involved), and this should have a minimal effect, as demonstrated by the ΔE value, which is very close to the one related to the case in which there are no P atoms in the migration channel. During diffusion, however, the sodium ion is in a condition where it interacts with two PO sites, which destabilizes the transition state and makes the energy barrier significantly higher than in the other cases. It is important to note that the diffusive process also affects the reverse migration (Na1→Na2); from the data reported in Table 2 it can be indeed seen that the mono-substitutions (in particular the one on σ_a site) have negligible influence on the reverse barriers, but these become significantly higher in the case of multiple substitutions, reaching ca. 20 kJ mol^{−1} for the tri-substituted system, sensibly affecting the E_b^{kr} value. It is therefore evident that the investigated NaSICON structure will work more efficiently if the Si/P substitutions are few and far between, i.e. at low phosphorus content.

3.4. Na⁺ migration with Zr vacancy

Let's now focus on the effect of a zirconium vacancy on the migration process. To do this, the Zr nucleus closest to the two Na1 and Na2 topological sites involved in the sodium migration was identified in the supercell. Conceptually, the aforementioned zirconium was eliminated from the system as a Zr⁴⁺ ion, and the resulting structure with four negative charges was relaxed. The optimized structure differs significantly from the input one since a sodium ion coming from a Na2 site takes over the position once occupied by the Zr⁴⁺ ion, forming a structure where a positive charge is located in a region of such high electronic charge density. Table 3 reports the volumes of the octahedral cavities defined by the oxygen atoms around the sites involved in the sodium migration process in the supercell structures obtained from the possible combinations of presence/absence of Na and Zr ions.

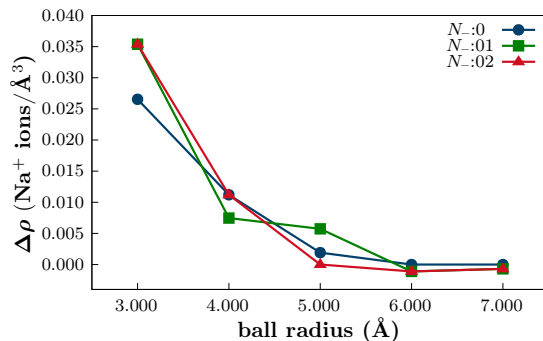


Figure 3: The Na⁺ ion density variation ($\Delta\rho$) occurring around the site where a zirconium vacancy is created in the systems $N_{-}:0$, $N_{-}:01$ and $N_{-}:02$ with respect to the pristine $N_{+}:0$ NaSICON structure.

Here we note that the disappearance of Zr has a significant impact on the distortion of the local region, with an increase of more than 5 Å³ in the volume of the Zr cavity. The distortions are reflected, albeit to a limited extent, in the cavities around the Na1 and Na2 sites; in particular, when sodium vacancies are present (the Na1 site in the $N_{-}:01$ system and the Na2 site in the $N_{-}:02$ system), a significant decrease in the octahedral volume is calculated. This may be due to the accumulation of sodium ions in the Zr vacancy region. In order to quantify the crowding above, it can be helpful to take a look at Figure 3, where the Na⁺ ions density around the Zr₄⁺ vacancy (expressed as variation, $\Delta\rho$, with respect to pristine NaSICON) is reported for the three $N_{-}:0t$ systems. At long distances $\Delta\rho = 0$ for the $N_{-}:0$ system, while for the $N_{-}:01$ and $N_{-}:02$ cases the slight decrease in density is merely due to the effective lack of a sodium ion in these computational models. On the other hand, at short and medium distances (up to more than 5 Å) there is a notable increase in the local density of Na⁺. In the diffusion channel region, in particular, up to four more sodium ions can be found than in the stoichiometric counterpart, obviously attracted by the high negative charge density left by the zirconium vacancy. In details, regarding the fully relaxed $N_{-}:01$ structure, it was observed that: a) the sodium ions in the first coordination sphere around the Na1 site approach the octahedron of oxygen atoms that remained vacant in the central sodium, but they do not get inside it; b) a sodium ion in the neighborhood approaches significantly the octahedron of O atoms surrounding Na2. As regards the $N_{-}:02$ structure, instead, c) the vacant Na2 site has been taken by another sodium ion coming from a vicinal Na1 site, and consequently the oxygen octahedral cage surrounding the now vacant Na1 site undergoes strong distortions.

We can imagine that, in such a situation, the diffusion of sodium ions is strongly inhibited. As a matter of fact, calculations show that the $N_{-}:01 \rightarrow N_{-}:02$ process occurs by means of a concerted migration of the kind Na1→Na2→Na1(vacant), i.e. Na1 takes the place of Na2 which simultaneously moves towards the vacant site of

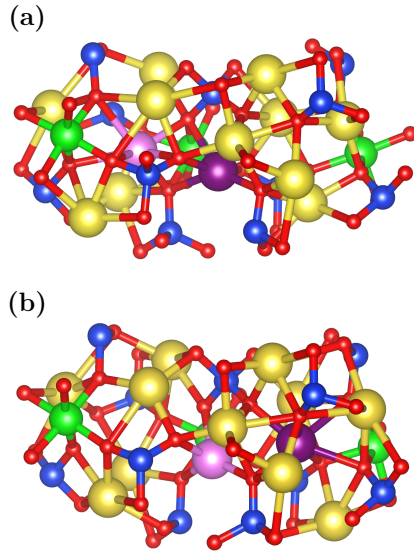


Figure 4: The local portions of the (a) $N_{-}:01$ and (b) $N_{-}:02$ NaSICON systems involved in the concerted effective $\text{Na1} \rightarrow \text{Na1}$ diffusion of sodium ions in the presence of a zirconium vacancy. The involved Na^{+} ions are highlighted in pink and purple.

another Na1 site, with the net effect of having a global migration of the kind $\text{Na1} \rightarrow \text{Na1}$. For this concerted process an energy barrier of 68.3 kJ mol^{-1} was calculated, which is one order of magnitude higher than the one observed for the $N_{+}:01 \rightarrow N_{+}:02$ case, where the Zr^{4+} ion is present. Since this energy gap is so large that it cannot be compensated by the small energy changes induced by possible Si/P substitutions, whose effect on energy is much more limited, systems simultaneously containing phosphorus and zirconium vacancies in the migration channel have not been investigated.

Table 3

Volumes of the main cavities involved in the sodium migration process in the presence and absence of a Zr^{4+} vacancy in the diffusion channel.

System	Volume/ $\text{\AA}^3$		
	Na1 site	Na2 site	Zr site
$N_{+}:0$	17.829	16.150	12.203
$N_{-}:0$	18.218	16.807	17.882
$N_{+}:01$	19.875	16.760	12.180
$N_{-}:01$	19.778	17.042	17.363
$N_{+}:02$	18.121	18.300	12.209
$N_{-}:02$	18.571	17.590	17.566

4. Conclusions

The activation energies for the diffusion of sodium ion between two adjacent cages belonging to the selected non-stoichiometric NaSICON system models with different local

proportions of silicon and phosphorus were obtained. The general trend shown by the reported DFT results is that the activation barriers associated to the Na diffusion process are lower than those reported in the literature for similar systems, and that the entire energetics extends within a narrow window of values. This is likely due to the dimension of the supercell used in this study, which would guarantee adaptability to distortions during Na^{+} migration and minimize the fictitious forces due to the periodic repetition of the defects.

On the basis of the energetic characteristics of diffusion, interpreted in atomistic terms, it can be stated that an even more efficient NaSICON (in terms of kinetically resolved activation energy) could be obtained if the energy barrier for the diffusion of sodium from the here termed Na1 to the Na2 site is reduced, being the barrier for the reverse process (which reaches a minimum of 3.4 kJ mol^{-1}) already highly favorable to sodium migration. This could be achieved, for instance, by substituting zirconium with a different metal. The investigation of these new NaSICON systems is a natural extension of the present work.

Two final considerations deserve attention. Zirconium vacancies are in fact detrimental to the migration process. It is true that the calculated high migration barrier must be interpreted within the context of the charged model employed but, while the exact local structural features might adapt under macroscopic, fully compensated conditions, the result demonstrates a qualitative characteristic behavior: the high negative charge density induces a localized crowding of sodium ions, establishing that zirconium vacancies could act as effective electrostatic traps that severely inhibit diffusion. Moreover, an accuracy high enough to ensure good confidence in the results has been achieved. However it is to note that, while the large supercell employed (having a volume of ca. $9000 \text{ \AA}^3$) helps to minimize periodic artifacts, the computational models used describe specific local environments, meaning that the effects of macroscopic configurational disorder and defect concentrations are not fully captured. Consequently, the present conclusions are restricted to the local migration energetics of the investigated pathways. Nevertheless, by isolating the specific impacts of Si/P substitutions and Zr vacancies on individual Na^{+} jumps, this work establishes useful energetic parameters for future simulations, based e.g. on percolation models or kinetic Monte Carlo, aimed at predicting macroscopic ionic conductivity.

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CRedit authorship contribution statement

Marco Bertini: Software, Investigation, Data curation, Writing - Original draft preparation. **Francesco Ferrante:** Conceptualization, Methodology, Investigation, Data curation, Writing - Review and Editing. **Dario Duca:** Funding acquisition, Data curation, Writing - Review and Editing.

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