First-principles study of the structural stability and electrochemical properties of Na$_2$MSiO$_4$ (M = Mn, Fe, Co and Ni) polymorphs†

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Sodium orthosilicates Na$_2$MSiO$_4$ (M = Mn, Fe, Co and Ni) have attracted much attention due to the possibility of exchanging two electrons per formula unit. They are also found to exhibit great structural stability due to a diamond-like arrangement of tetrahedral groups. In this work, we have systematically studied the possible polymorphism of these compounds by means of density functional theory, optimising the structure of a number of systems with different group symmetries. The ground state is found to be Pc-symmetric for all the considered M = Mn, Fe, Co, Ni, and several similar structures exhibiting different symmetries coexist within a 0.3 eV energy window from this structural minimum. The intercalation/deintercalation potential is calculated for varying transition metal atoms M. Iron sodium orthosilicates, attractive due to the natural abundance of both materials, exhibit a low voltage, which can be enhanced by doping with nickel. The diffusion pathways for Na atoms are discussed, and the relevant barriers are calculated using the nudged elastic band method on top of DFT calculations. Also in this case, nickel impurities would improve the material performances by lowering the barrier heights. Notably, the ionic conductivity is found to be systematically larger with respect to the case of lithium orthosilicates, due to a larger spacing between atomic layers and to the non-directional bonding between Na and the neighbouring atoms. Overall, the great structural stability of the material together with the low barriers for Na diffusion indicates this class of materials as good candidates for modern battery technologies.

In recent years, Na-ion batteries have attracted increasing interest from the scientific community. They are considered the most attractive alternative to Li-ion batteries, due to the low cost and widespread abundance of sodium. Electrode materials research is following a strategy analogous to the Li-ion case, investigating the structural and diffusive properties of layered oxides, phosphates and titanates. The family of intermetallic lithium orthosilicates Li$_2$MSiO$_4$, where M = Mn, Fe, Co, and Ni, has been the focus of several studies due to the possibility of exchanging two electrons per formula unit, which corresponds to theoretical capacities in excess of 300 mA h g$^{-1}$. However, this process is difficult to achieve and most experimental works report the extraction of only one ion. Furthermore, these materials exhibit a complex and rich polymorphism, and a phase transition is known to occur upon battery cycling, significantly decreasing the initial capacity of Li$_2$FeSiO$_4$.

More recently, Na$_2$MSiO$_4$ compounds have been recognised as more promising candidates for novel cathode materials. It has been inferred by means of ab initio calculations that full extraction of Na ions is easier to achieve with respect to the case of lithium due to a lower deintercalation voltage plateau. Furthermore, the diffusion barrier for Na ions is found to be significantly lower. This trend is preserved for different structural phases and can be attributed to the larger equilibrium volumes predicted for Na-based compounds, which correspond to a weaker interaction between atomic layers with respect to the case of lithium orthosilicates. Notably, Na doping would improve the performance of a Li-based cathode due to this feature. Na-based orthosilicates are also known to exhibit greater structural stability upon cycling with respect to their lithium counterparts, due to the high Na/Fe exchange barriers observed for equilibrium structures exhibiting a diamond-like arrangement of AO$_4$ (A = Fe, Si) tetrahedral blocks. DFT studies of these structures report also a very small volume change (below 3%) upon complete desodiation. Experimental studies are overall in agreement with the predicted structural stability, only when control over impurities is achieved. In 2011, Duncan and coworkers first successfully synthesised Na$_2$MnSiO$_4$ (space group Pc) using a sol–gel method. Chen and coworkers synthesised Na$_2$MnSiO$_4$ following the same procedure, and measured a
reversible capacity of 125 mA h g\(^{-1}\), which is the first evaluation of the electrochemical properties of Na-based orthosilicate cathodes. More recently, Na\(_2\)CoSiO\(_4\), prepared via a hydrothermal method, was used as positive electrode material for Na-based capacitors and sodium iron orthosilicate Na\(_2\)FeSiO\(_4\) was synthesized and reported to exhibit a reversible electrochemical activity of 106 mA h g\(^{-1}\). The latter material is particularly attractive due to the natural abundance of both sodium and iron. Another study reports the synthesis of Na\(_2\)FeSiO\(_4\) in an impure form (85%) with Na\(_2\)SiO\(_3\) as the major impurity. A specific capacity of 126 mA h g\(^{-1}\) has been measured in this case. Treacher and coworkers investigated the diffusion rates of a Na\(_2\)CoSiO\(_4\) cathode, synthesised using a novel co-precipitation method. The experimental results indicate the presence of two polymorphs, corresponding to Pc and Pbca space groups. A reversible specific capacity larger than 100 mA h g\(^{-1}\) is measured. Numerical simulations, based on an empirical interatomic potential, predict a very stable structure with rare occurrence of Na/Co anti-site defects, in agreement with the first-principles calculations of Na\(_2\)FeSiO\(_4\). In this work, we investigate the configurational space of Na-based orthosilicates by means of density functional theory, with the aim of exploring the possible polymorphism of these compounds (Section 2). We analyse a variety of structures, corresponding to different space groups and exhibiting a diamond-like structure for tetrahedral blocks which is at the base of their excellent structural stability. This study is carried out for different transition metals M = Mn, Fe, Co, Ni. In each case, the ionic ground state is found to be Pc-symmetric, in agreement with the experimental observation for Mn and Co. The results for Fe indicate a more complex polymorphism: experimental samples compatible with the Pc space group are reported in ref. 14, but more complex structures are observed in other works. Our analysis is extended (Section 3) to the study of bonding properties and charge transfer, in order to provide a physical-chemical insight into the interactions between Na, Si, Fe and their nearest neighbours (O atoms). We thus proceed to study the average voltage of sodium deintercalation/intercalation for the ground-state geometry as a function of the transition metal atom M (Section 4). Finally, we explore the possible diffusion paths for Na in iron orthosilicates, and provide the barrier height for this process for varying transition metal atoms.

**1 Computational details**

Total energies are calculated using the projected-augmented plane-wave (PAW) implementation of Vienna ab initio simulation package (VASP). Calculations are performed using the Perdew–Burke–Ernzerhof (PBE) functional for the exchange–correlation term, with the Hubbard parameter correction (GGA+U), following the rotationally invariant form. This approach is known to provide accurate results for lithium orthosilicates, often in line with the computationally more expensive HSE06 approach. Effective U values for the d states of Mn, Fe, Co, and Ni are chosen to be 4.0, 2.7, 5.0 and 5.1 eV, respectively. The effective on-site exchange interaction parameter J is fixed to 1 eV. These values yield to a good agreement with experimental reports in the Li case. We note that a larger U value (4 eV) is reported in the literature for the Na\(_2\)FeSiO\(_4\) system. Test calculations for a Pc-symmetric system show that this different choice for U would not affect the structural properties of this material, but only produce a 0.3 eV shift in the bandgap energy, for which the experimental measurement is not available. Moreover, the energy difference between a Pc-symmetric and a C\(_2\)v-symmetric structure is the same for these two U values, indicating that the shift in energy is likely to be the same for all the considered geometries. The robustness of the results for varying U values for the Pc-symmetric Na\(_2\)CoSiO\(_4\) structure is also checked. The energy–volume curves obtained at U = 5.1 eV, 5.5 eV, and 6.0 eV produce the same fitting parameters to the equation of state.

The optimised structures are obtained by minimising both the stress tensor and the Hellmann–Feynman forces, using the conjugate-gradient algorithm with an energy convergence threshold of 10\(^{-3}\) eV. Brillouin zone (BZ) integration is performed with \(\Gamma\)-centred Monkhorst-Pack grids, using an electronic smearing following the Methfessel– Paxton method, with a gaussian broadening of 0.2 eV. The size of the grid depends on the cell volume and on its shape. It is found that an energy convergence within 1 meV is obtained using a resolution of 0.15 Å\(^{-1}\) in reciprocal space and a 500 eV kinetic energy cutoff for the plane wave expansion. For each of the considered structures, a complete geometry optimisation (cell shape and volume, atomic positions) is performed, followed by the application of a tensile/compressive diagonal strain to obtain the total energy of the system as a function of volume for a fixed cell shape. We use 3 increments in both tension and compression, each corresponding to a 1% volume update. The resulting energy profile is then fitted to the Murnaghan equation of state. Both ferromagnetic (FM) and anti-ferromagnetic (AFM) calculations are carried out for the Pc-symmetric Na\(_2\)FeSiO\(_4\) system. Equivalent results are obtained, with a total energy difference lower than 2 meV, well below the accuracy threshold of DFT. Moreover, the magnetic moment for a Fe atom calculated from the site-projection of d orbitals is found to be 3.59 \(\mu_\text{B}\) in both FM and AFM cases. In the rest of the paper, only the results of FM calculations are presented.

The electronic density of states (DOS) and the site-project density of states (PDOS) are evaluated using the tetrahedron method with Blöchl corrections for BZ sampling. This method is known to provide accurate DOS profiles, avoiding the negative occupancy resulting from the Methfessel–Paxton gaussian broadening. The band gap values are evaluated from the so-obtained DOS as the distance on the energy axis between the maximum of the valence band and the minimum of the conduction band. It is well known that the band gap values of solids obtained from standard DFT calculations are systematically underestimated due to discontinuity in the exchange–correlation potential. These values are typically 30–50% smaller than the experimentally measured ones and exhibit a strong dependence on the approximations used for the exchange and...
correlation terms. In the present work, due to the large number of compounds involved, we have limited ourselves using the GGA+U approximation. The atom-resolved charge transfer is calculated via the Bader decomposition scheme, and the covalency of the bonding is discussed studying the electron localisation function (ELF).

The average Na-intercalation voltage is calculated as:

\[
V(x_1, x_2) = \frac{E(x_2) - E(x_1) - (x_2 - x_1)\mu}{x_2 - x_1}
\]

where \(x_1\) and \(x_2\) are the number of Na atoms in the unit cell and \(E(x)\) is the total energy. The chemical potential \(\mu\) accounts for the different stoichiometry, and it fixed to the total energy of a bcc Na crystal. The total energy of the defect-free Na\(_2\)MSiO\(_4\) system is always used as a reference. This approach has been successful is studying the voltage trend in several families of materials with the transition metal atoms M ranging from Mn to Ni, including olivine LiMPO\(_4\), MgMSiO\(_4\), Li\(_2\)MSiO\(_4\), and LiMVO\(_4\).

The Na diffusion barrier height is calculated using the nudged elastic band (NEB) method. A supercell is used to ensure a large separation between repeated images, and five replicas of the system are created by linear interpolation between the initial and final states. A NEB calculation is then performed to obtain a guess for the minimum energy path (MEP). After convergence, the calculation is restarted, using the climb-image method to improve the estimate for the barrier.

The optimisation of intermediate images is carried out using the FIRE algorithm with a force convergence threshold of 50 meV Å\(^{-1}\). The more general solid-state NEB approach, which allows the lattice degrees of freedom together with the atomic positions to be relaxed, has been tested on a Na\(_2\)FeSiO\(_4\) system. We found only a small contribution to the energy barrier (50 meV, comparable to the typical accuracy of DFT energy barriers and smaller by an order of magnitude than the climb-image contribution of 160 meV). This contribution is therefore neglected in this work. The so-evaluated energy barrier \(E_b\) is used together with the Na–Na hopping distance \(b\) to evaluate the diffusion coefficient using the relation

\[
D = D_0 \exp\left( -E_b/k_B T \right)
\]

where \(k_B\) is the Boltzmann constant, \(T\) the temperature and \(D_0\) the attempt frequency, assumed to be 100 Hz.

The Atomic Simulation Environment (ASE) is used for converting input/output formats and data analysis. Ball-and-stick and tetrahedral models are rendered using VESTA; data-grids for charge density and the electron localisation function are visualised using XCrySDen. Plots are generated using gnuplot.

### 2 Structural stability

In this section, we present the results of first-principles calculations aimed at the identification of structural minima for sodium orthosilicates. The optimal cell parameters are calculated starting from different symmetries, and the total energies are compared in order to identify the ionic ground state. We focus on 12 structures characterised by a diamond-like Fe–Si network, composed by only tetrahedral AO\(_4\) (A = Fe, Si) blocks, shown to exhibit great structural stability. Each structure is labelled using its space group number. This study is carried out for Na\(_2\)MSiO\(_4\) orthosilicates, for M = Mn, Fe, Co, and Ni, following the procedure detailed in Section 1. The structural parameters for M = Fe are reported in Table 1 and the corresponding energy–volume curves are displayed in Fig. 1. Equivalent data for M = Mn, Co, and Ni can be found in the ESL.

The structural optimisation can modify the starting symmetry of the system. In this work, we have identified 8 (meta)stable configurations, shown in Fig. 2 using coordination polyhedra. The \(Pmn2_1\)-modi and \(Pmn2_1\)-ncycled structures relax to similar \(Pc\)-symmetric configurations. Even though these structures are equally stable and the predicted equilibrium volume is the same, the \(b/a\) and \(c/a\) ratios are different. This does not influence the crystal properties within the typical DFT accuracy. The \(P2_1\)-ncycled

<table>
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<tr>
<th>Space gr.</th>
<th>Initial</th>
<th>Optimised</th>
<th>(E) (eV)</th>
<th>(V) (Å(^3))</th>
<th>(B) (GPa)</th>
<th>(B')</th>
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<tr>
<td>(Pc) (7)</td>
<td>(Pc) (7)</td>
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<td>104.80</td>
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<tr>
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<tr>
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<tr>
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<td>105.56</td>
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<td>(Pmn2_1) (33)</td>
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<td>104.34</td>
<td>76.68</td>
<td>4.90</td>
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<td>(C22_1) (20)</td>
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<td>106.98</td>
<td>75.73</td>
<td>4.89</td>
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<tr>
<td>(P2_1) (4)</td>
<td>(P2_1) (14)</td>
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<td>105.09</td>
<td>75.49</td>
<td>5.67</td>
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<tr>
<td>(P2_1) (14)</td>
<td>(P2_1) (14)</td>
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<tr>
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<td>(Pmmm) (62)</td>
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<td>(P3_1) (159)</td>
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<td>0.49</td>
<td>102.40</td>
<td>85.78</td>
<td>4.40</td>
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</table>

![Fig. 1 Energy–volume curve for stable Na\(_2\)FeSiO\(_4\) structural minima, labelled using the symmetry of the optimised configuration. The zero energy is fixed to the minimum of the \(Pc\) curve.](image-url)
structure relaxes to a local minimum corresponding to a \( Pc \)-symmetric configuration. Another unstable phase corresponds to the \( P2_1/c \) group, which relaxes into \( P2_1/c \).

We note that all the minima obtained are within an energy window of 0.3 eV from the ionic ground state \( Pc \) (with the only exception of \( P3_2 \), greatly unfavourable especially in the case of Mn and Co). Moreover, the calculated equilibrium volumes are very similar, indicating great structural stability in spite of the observed polymorphism. We also note that the ordering of the energies is conserved for varying \( M \), indicating that the observed structural stability would be preserved by doping of the material, relevant to battery materials e.g. for tuning the voltage. The examined structures exhibit small values of bulk modulus (soft materials). This is the mechanical consequence of their characteristic porous structures, and phase transitions may therefore occur, even at moderate pressure.

Our results are consistent with the literature. In ref. 19, the experimental structure of \( \text{Na}_2\text{CoSiO}_4 \), synthesised using both co-precipitation and solid-state synthesis, is compatible with the \( Pc \) space group. The parameters for the elementary cell, obtained from X-ray diffraction (XRD) patterns, are reported in Table 2 and compared with our simulations. A good agreement is observed, as the deviation between the experimental and the theoretical values for lattice parameters is below 2%. Notably, all the three \( Pc \)-symmetric minima found, starting from \( Pc, \text{Pmn}2_1, \text{Pm} \) and \( \text{Pmn}2_1 \)-ncycled, are consistent with the experimental measurement. The structural parameters for these structures are reported in Table 3 and in the ESI.†

In ref. 20, \( \text{Na}_2\text{MnSiO}_4 \) is synthesised using the sol–gel method, and a \( Pc \)-compatible structure is obtained. The experimental data, reported in Table 2, are in agreement with our results. In the case of iron orthosilicates, different experimental observations are reported in the literature. In ref. 15, the XRD patterns would suggest a cubic cell with space group \( F4 \). First-principles calculations do not predict the existence of such a structure,\(^{13}\) and the experimental structure is rationalised as an ensemble average of \( P2_13, C222_1 \) and \( C2 \) phases. In another experimental work\(^{14} \) on \( \text{Na}_2\text{FeSiO}_4 \), the sample is compatible with the \( Pc \) space group. The results from this reference are reported in Table 2 and are in excellent agreement with our calculations. Note that our prediction of stable structures exhibiting \( C2 \) and \( C222_1 \) symmetries (Table 1) partially supports the experimental observations in ref. 15.

### 3 Chemical properties

#### 3.1 Density of states and band structure

In this section, we provide further insight into the electronic properties of the \( Pc \)-symmetric \( \text{Na}_2\text{FeSiO}_4 \) compound. The total density of electronic states, calculated following the procedure described in Section 1, and the band structure along a high-symmetry path in the BZ are reported in Fig. 3. The Fermi level \( E_F \) is conventionally fixed to 0 eV, and separate plots are shown for the spin-up and spin-down channels, in panels (a) and (b), respectively. These channels present similar features. Very localised states are observed in the \( -6 \) eV region. Magnetic effects are not very important here, as only a small energy shift (\( \sim 0.5 \) eV) between the channels is observed and the shape of the peaks is
very similar, indicating a low contribution from the (strongly
magnetised) d states of the Fe atom. The region between −6 eV
and the Fermi level comprises the majority of valence states,
including a large contribution from the Fe d states. Magnetism
has therefore a large impact on this area. The spin-up channel
exhibits several non-localised peaks, distributed between
−5.5 eV and −2.3 eV. In the spin-down channel instead four
distinct peaks are observed. The first three are distributed
between −5 eV and −3 eV, and are separated from the fourth
one by a 3 eV gap. The two semi-degenerate valence bands are
the only contributors to this last peak.

The unoccupied states have a different distribution between
the two spin channels. Spin-up electron states are not localised,
and the overall contribution to the density of states is negligi-
gible. Unoccupied spin-down states are instead denser in the
region between 1.5 eV and 3 eV, where the major d peaks of the
DOS are observed. The minimum of the conduction band is
observed at the Γ point for both spin channels. The valence band
for the spin-down channel is constant along the path between Z
and Γ, where it exhibits its maximum value. The band gap can
therefore be identified as a direct one at the Γ point, but indirect
Z-Γ transitions are also favourable. Another maximum of the
valence band is observed at an intermediate distance between E
and C, lower in energy with respect to the value at Γ by less than
10 meV. The band gap for these transitions is 1.23 eV, much
lower than that observed for the spin-up channel (at least 2.5 eV).
The presence of a small band gap (see also Table 4), qualifies this
material as a semi-conductor. Note that this value is expected to
underestimate experimental measurements, as discussed in
Section 1. The electronic structure of Na₂FeSiO₄ is further
analysed by calculating the site-projected density of states, dis-
played in Fig. 4.

As previously observed, Fe d states, shown in panel (a),
provide only a minor contribution at energy values lower than
−5.5 eV. Their peaks are observed at very important energy
values: −2 eV and −0.1 eV, marking the valence band of both
spin-up and spin-down channels, and 1.5 eV marking the
conduction band of the spin-down channel. Given the abun-
dance of d states at these values, transitions from the valence to
the conduction band are more likely for these electrons, in
accordance with the metallic nature of bulk Fe. Comparison
between the PDOS of Fe and O, shown in Fig. 4, panels (a)
and (c), provide information about the bonding between these
two atoms. A degree of covalency can be expected from the
degeneracy at −2 eV between Fe d-electrons and O p-electrons,
corresponding to the majority of d states in the spin-up
channel. On the other hand, the PDOS for the two elements
are very different for the spin-down channel due to the lack of
magnetisation of the O atom. The spin-up channels, apart the
aforementioned peak, also present different shapes. We can
therefore expect the Fe-O bonding to be prevalently non-
directional, and to have an ionic character in virtue of the
charge transfer expected in this material and calculated in
Section 3.2.

The opposite behaviour is observed for the Si–O bonds in
Fig. 4, panels (c) and (d). The two peaks observed for silicon at
−8 eV (s states) and −5.5 eV (p states) are degenerate with the
peaks of the first two p states of oxygen, as can be observed
comparing panels (c) and (d) in Fig. 4. This is a clear sign of
covalent bonding. The Si atom also presents scarcity of
states at the Fermi level, so that electronic transitions are very
unlikely. The Na–O bonding exhibits instead a low level of
covalency. While some degeneracy is present (peaks at −5.5 eV

Table 4 Band gap values for the examined systems, labelled according to
space groups

<table>
<thead>
<tr>
<th>Space group</th>
<th>Band gap (eV)</th>
</tr>
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<tbody>
<tr>
<td>Mn</td>
<td>2.37, 1.23</td>
</tr>
<tr>
<td>Fe</td>
<td>3.02, 2.44</td>
</tr>
<tr>
<td>Co</td>
<td>2.35</td>
</tr>
<tr>
<td>Ni</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3 Total density of states and band structure along a high symmetric
path in the BZ for the Pc-symmetric Na₂FeSiO₄ phase. The data for the two
spin channels (up and down) are plotted separately in panels (a) and (b),
respectively. The Fermi level E_F is indicated with a red line.

Fig. 4 Calculated site-projected density of states for the Na₂FeSiO₄ phase
in Pc-symmetry. The relevant states for Fe, Na, O, and Si are shown in panels
(a), (b), (c) and (d), respectively. The spin-down channel is conventionally
plotted on the negative y axis. The Fermi level E_F is indicated with a red line.
and \(-2\) eV), the major contribution of Na to the density of states is at \(-5\) eV for both spin channels. A similar peak is also observed for the spin-up channel of Ni, indicating a non-negligible interaction between these two atoms. This is compatible with their interatomic distance of 3.24 Å. The overall bonding of Na atoms is expected to have a Na–O ionic component and Na–Fe interactions, probably of metallic character. Overall, directional bonding is not expected to occur, in agreement with the excellent ionic conduction properties observed in Section 4.

A full chemical characterisation of all the compounds examined in Section 2 is out of the scope of this work. We limit ourselves to calculate the band gap for the examined systems, reported in Table 4. The band gap is shown to have a significant dependence on the transition metal atoms. The iron-based system is characterised by a low value for the band gap, which drastically increases by a factor of 2 for stable but energetically unfavourable compounds exhibiting \(P2_1/c\) symmetry. The other compounds exhibit systematic larger band gap values in the order Co > Ni > Mn, with the only exception of the aforementioned \(P2_1/c\) case. We note grand stability in the magnetic moment, which conserves the reference value for the isolated atom in all the examined cases.

3.2 Charge transfer and bonding

The study of the equilibrium \(Pc\)-symmetric phase of Na\(_2\)FeSiO\(_4\) is presently further enriched by analysing the charge redistribution in the system and by further characterising the bonding. The charge density plot is displayed in Fig. 5, panels (a) and (d), for two different \(z\) planes, containing Na, O, Si and Na, O, Fe atoms, respectively. The maxima of the charge density are observed at the Fe atoms sites. This is easily understood by virtue of the larger number of valence electrons (8) with respect to the other atomic species considered (1, 4 and 6 for Na, Si and O, respectively). Notably, charge peaks in correspondence to O atoms are comparable to Fe ones, indicating a charge transfer process. The Na atoms in both panels (a) and (d) are indistinguishable from the background, indicating charge depletion from this site. These observations are confirmed by the charge density difference, calculated with respect to a reference superposition of atomic orbitals, displayed for the same atomic planes in Fig. 5, panels (c) and (f). Charge depletion is observed.

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**Fig. 5** Charge density (a and d), charge difference (b and e) and electron localisation function (c and f) plots for the optimised Na\(_2\)FeSiO\(_4\) \(Pc\)-symmetric phase. Two different atomic \(z\) planes are shown containing Fe, Na, O (a–c) and Si, Na, O (d–f) atoms, respectively.
4 Electrochemical properties

4.1 Average intercalation potential

In this section, we analyse the consequences of the electronic properties previously characterised by calculating the electrochemical features, thus providing insight into the application of such materials as cathodes for Na-ion batteries. As a first step, the volume change of these structures upon Na deintercalation is calculated. This provides crucial information about the structural stability of the materials upon battery cycling. The equilibrium volumes, calculated as a function of the Na density following the structural optimisation recipe detailed in Section 1, are displayed in Fig. 6. The overall volume variations are always below 4%, with the only exception of the M = Mn system, for which the cell monotonically shrinks upon Na deintercalation down to a 10% variation with respect to the starting volume. In the other cases, the volume of the cell shrinks upon removal of the first Na atom per formula unit. In the fully desodiated case, the volume is always within 2% from the starting value. This is in good agreement with ref. 12, in which a 2.5% decrease is observed for NaFeSiO₄ and no variation is found for the desodiated structure.

for both the Na and the Fe atoms, and it is larger in the latter case, while the O atoms gain a significant amount of electrons. The Bader decomposition is used to quantify this charge transfer, reported in Table 5. The Fe and Na atoms are found to be depleted, while O atoms gain electrons consistently as observed in Fig. 5. The larger gain of the O₁ atom is explained by its short distance from the Na₂ atom (2.27 Å, to be compared with the average value of 2.31 Å). The Fe–O bond is found to be prevalently ionic.

A small covalent (directional) component is however present, as can be appreciated from the charge transfer to the interstitial region between Fe and O observed in Fig. 5, panel (c). The charge distribution around the Na atom is spherically symmetric. The Na–O bonding can be therefore identified as pure ionic. The greater ionicity of Na–O with respect to Fe–O is compatible with the electronegativity difference between these atoms. In the Si–O case, the interaction is mainly covalent, as can be observed from the negligible charge transfer for Si and the lack of spherical symmetry for the charge distribution pertaining to the oxygen atom.

A further level of analysis is provided by the electronic localisation function (ELF). In a many-electron system, the ELF, positive and smaller than 1 by construction, can be shown to have its maximum values in regions where bonding between electrons exhibits covalent nature, or for unpaired electrons (directional dangling bonds). The ELF is a constant by definition in the case of a homogeneous electron gas, with this value chosen to be 0.5. The values of this order indicate the metallic character of the bonding. In this system, the ELF reaches the maximum value of 0.72, indicating the lack of pure covalent interactions. Contour plots for this quantity are shown in Fig. 5, panels (b) and (e).

The ELF exceeds the value of 0.5 only in correspondence to O atoms. This is an expected feature, given their large electronegativity. Larger values of ELF can be noticed in the proximity of the Si atom, indicating a pronounced covalency. Notably, the tendency to form a covalent bond is also observed for O–O pairs.

In the case of Fe atoms, smaller ELF values are observed. Owing to the large charge transfer between Fe and O, a repulsive interaction between O atoms is observed, marked by the polarisation of the ELF. The contribution from the Na atom is negligible. In fact, this atom is not distinguishable from the background. This is the footprint of pure ionic bonding, and complements the observations from Section 3.1 and Fig. 4.

Table 5 Atom-resolved charge transfer for Pc-symmetric Na₂FeSiO₄ as evaluated by Bader decomposition. A superposition of atomic orbitals is used as a reference. The atom notation is consistent with Table 3.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Fe1</th>
<th>Na1</th>
<th>Na2</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge</td>
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<td>-0.44</td>
<td>-0.45</td>
<td>+0.00</td>
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</table>

<table>
<thead>
<tr>
<th>Atom</th>
<th>O1</th>
<th>O2</th>
<th>O3</th>
<th>O4</th>
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<tbody>
<tr>
<td>Charge</td>
<td>+0.65</td>
<td>+0.41</td>
<td>0.51</td>
<td>0.59</td>
</tr>
</tbody>
</table>

Fig. 6 Percentage variation of equilibrium volume for desodiated structures (a) and the corresponding deintercalation/intercalation voltage (b) for Pc-symmetric orthosilicates.

Fig. 7 Top (a) and side (b) views of the Pc phase. Only bonds between Na atoms (yellow) are shown in order to provide a clearer view of the diffusion channels. The Fe, Si, and O atoms are indicated with red, blue and grey spheres, respectively. The sites occupied by the vacancy along the considered paths are marked with roman numbers. The bond length of single steps are shown in panel (c) for the M = Fe case, together with the calculated barrier heights.
The structural stability of Na-based orthosilicates is hereby verified, and only a weak dependence on the M element is found, indicating that the inclusion of metallic impurities in the cathode (useful e.g. for tuning the battery voltage) would not destabilise the overall structure.

The total energies resulting from the volume optimisation of these systems can be used to evaluate the average voltage of sodium deintercalation/intercalation (see eqn (1)). These values are displayed in Fig. 6(b). The $M = Fe$ compound exhibits the lowest value of the series. This is in line with known results for Li orthosilicates, and for Na ones with $Pmmn_2$ symmetry. The calculated extraction energies for the first and the second atom, respectively, 2.1 eV and 4.3 eV, are in good agreement with values encountered in the literature (about 2 eV/4.4 eV for $Pmmn_2$, $C22_1$, and $Pc$, while $C2$ is found to have a lower value of about 1.6 eV/4.4 eV). 

### 4.2 Ionic conductivity

The diffusion properties of Na atoms in the equilibrium phase are investigated using the NEB method, as detailed in Section 1. A $2 \times 2 \times 2$ supercell of the original structure is used, corresponding to 16 formula units and to a distance of at least 10 Å between repeated images of the vacancy. Two non-equivalent Na lattice sites can be distinguished in the supercell, as shown in Table 3. We have here considered two different paths connecting two equivalent sites as shown in Fig. 7.

This intermediate state is least energetically favoured compared to the starting point. The values for this total energy difference for different compounds are 0.25 eV, 0.11 eV, 0.18 eV, and 0.04 for Mn, Fe, Co and Ni, respectively. The initial site for the vacancy is labelled (i) in Fig. 7(a and b), the intermediate state is (ii) and the final states are (iii) and (iv), respectively. Note that these final states are both equivalent to (i). The length of each path and the respective barrier for Na$_2$SiO$_4$ is reported in Fig. 7(c).

Notably, the minimum energy path presents a very asymmetric shape, as the barrier associated with the (i) $\rightarrow$ (ii) path is significantly smaller than either the one for (ii) $\rightarrow$ (iii) or (ii) $\rightarrow$ (iv). This trend is consistent between the examined compounds, and it has been already observed for the $M = Mn$ case. Given the similarity between the height of the energy barrier obtained for the cases (ii) $\rightarrow$ (iii) and (iii) $\rightarrow$ (iv) [almost the same, given the fact that the accuracy of the method is 0.1 eV], we have decided to neglect the calculation for the second path for the other compounds.

The results of NEB calculations for varying M are reported in Table 6. We notice that the asymmetry between the two barriers is preserved for varying M. The second part of the path, indicated as (ii) $\rightarrow$ (iii) is the limiting step. Iron orthosilicate exhibits the largest barrier among the group. The overall order is Fe > Mn > Co ≈ Ni. Ni doping is therefore predicted to enhance the ionic conductivity of the materials, without destabilising the crystal structure. This is due to the fact that the two materials have an ionic ground state presenting the same symmetry, and the difference in volume between equilibrium structures is 2%, as can be noted from Table 1. Moreover, the volume change difference between Ni and Fe sodium orthosilicates upon desodiation is also within 2%.

### 5 Conclusion

The structural and electrochemical properties of Na based orthosilicates Na$_2$MSiO$_4$ (M = Mn, Fe, Co, Ni) are investigated by means of density functional theory calculations. These compounds are characterised by a robust diamond-like M–Si network, which is known to provide great stability upon battery cycling. While many different phases can coexist (in a 0.3 eV energy window), the ionic ground state is shown to be $Pc$-symmetric for all the considered transition metal atoms M. The nature of the bonding is analysed by studying the density of electronic states, the charge distribution and the electron localisation function for Na$_2$FeSiO$_4$. The results indicate prevalently metallic bonding between Na and surrounding atoms, partially responsible for the lowest diffusion barrier observed in the case of lithium orthosilicates. The study of electrochemical properties reveal great cycling stabilities for Fe, Co and Ni orthosilicates (the volume change upon both partial and complete desodiation is below 5%), while Mn is under-performing, with volume change up to 10% upon complete desodiation. The calculated second Na deintercalation plateaus are lower than the respective values for Ni materials, indicating better possibilities for the extraction of two ions per formula unit, hardly achieved in the case of lithium orthosilicates. The Na$_2$SiO$_4$ compound is the most relevant from a commercial perspective, due to the abundance of both sodium and iron. This material is characterised by a low voltage (for the extraction of the first ion per formula unit) and by a smaller ionic conductivity with respect to the other compounds analysed in this work. This can be addressed by Ni-doping, which is predicted to both increase the voltage and decrease the diffusion barrier for a Na vacancy, without disrupting the excellent structural stability upon cycling of the material.

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References