

$\text{Na}_2\text{FeSiO}_4$ as a sodium-ion battery material: A computational perspective

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Abstract Polyanionic silicate-based cathode materials have attracted considerable attention due to their intrinsic structural stability, strong thermal and chemical resistance, and ability to achieve high operating voltages through the inductive effects of polyanion groups. In this study, atomistic simulations were conducted to explore the energetics of intrinsic point defect formation, Na-ion migration pathways, and dopant incorporation in $\text{Na}_2\text{FeSiO}_4$, providing key insights into its viability as a cathode material for sodium-ion batteries (SIBs). Among the native defects, the Na Frenkel pair exhibited the lowest formation energy, suggesting a natural preference for vacancy-mediated Na-ion migration. The calculated migration energy barriers of 0.38 and 0.41 eV further support the material's capability for efficient sodium-ion transport. Doping analysis identified K, Zn, and Ge as the most favorable isovalent dopants at the Na, Fe, and Si sites, respectively, while Ga showed a strong tendency to substitute at Fe sites and facilitate Na-vacancy formation. Furthermore, Al substitution at the Si site was found to increase the overall sodium content in the lattice. The electronic structure of these promising dopants was further investigated using density functional theory (DFT), offering deeper insights into their influence on the electrochemical behavior of $\text{Na}_2\text{FeSiO}_4$.

Keywords batteries, cathode, defects, density functional theory (DFT), diffusion

1 Introduction

Energy sources are fundamental to modern society, supporting essential daily activities, economic growth, and technological advancement. Although fossil fuels have historically dominated the global energy landscape, growing concerns about climate change and the unsustainable use of natural resources are accelerating the shift toward cleaner, more sustainable energy alternatives [2,3]. This global transition underscores the crucial role of renewable energy generation, which has become a primary focus of scientific research and innovation [3].

Rechargeable batteries are essential in this context, providing versatile and scalable energy storage solutions for a wide range of applications [4]. They are crucial for powering portable electronics, consumer devices, hybrid electric vehicles, and stationary grid storage systems,

especially for storing excess energy produced from renewable sources [5]. These diverse applications demand batteries with high volumetric and gravimetric energy densities, extended cycle life, large capacity, improved safety, and cost-effectiveness [6–8].

Although lithium-ion batteries (LIBs) currently dominate the market, they are not sufficient to meet the escalating global demand for rechargeable energy storage. The limited availability of lithium resources, their uneven global distribution, and the scarcity of essential battery materials underscore the need for alternative technologies [9,10].

Sodium-ion batteries (SIBs) have emerged as a promising alternative to LIBs, featuring comparable cell components and electrochemical mechanisms, with the primary difference being the use of Na^+ ions as charge carriers [11–13]. The high natural abundance, wide geographic distribution, and low cost of sodium contribute to the sustainability and economic viability of SIBs, making them particularly suitable for large-scale energy storage and grid-related applications [14].

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Polyanionic-type cathode materials have garnered significant attention owing to their structural flexibility, high ionic conductivity, excellent thermal stability, and robust three-dimensional frameworks [15]. These materials are generally expressed by the formula Na_xM_y(XO₄)_n, where X represents elements such as S, P, Si, As, Mo, or W, and M denotes a transition metal. The structure is composed of (XO₄)_n tetrahedral units and their derivatives, which form a strong covalent network [16]. This interconnected framework provides outstanding thermal and structural stability, contributing to improved safety and extended cycle life during battery operation [16]. Moreover, their open-framework architecture promotes fast sodium-ion transport and effectively mitigates volume changes during ion insertion and extraction processes, making them particularly well-suited for sodium-ion battery applications [15,16].

In a recent experimental study, Na₄VMn(PO₄)₃ was explored as a promising cathode material, with particular focus on enhancing its electrochemical performance through Sn doping at the V site [17]. Modulating the electronic structure has been shown to effectively facilitate sodium compensation in cathode organic additives, offering a promising strategy to enhance the electrochemical performance of SIBs [18].

Among polyanionic materials, sodium orthosilicates, Na₂MSiO₄ (M = Fe, Mn, Co, Ni), stand out as promising cathode candidates due to their natural abundance, low cost, and non-toxic composition [19,20]. The robust Si–O bond network ensures exceptional thermodynamic stability, allowing them to operate at temperatures up to 1000 °C with minimal volume variation (less than 5%) during sodium extraction. These properties make them ideal for high-temperature energy storage systems. In particular, disodium iron(II) silicate (Na₂FeSiO₄) has emerged as a strong contender due to its high theoretical capacity of 276 mAh/g, achievable via a two-electron redox process, positioning it as a promising material for next-generation energy storage solutions [16,19,20].

Extensive research has been conducted on various polymorphs of Na₂FeSiO₄, including monoclinic, triclinic, cubic, and orthorhombic forms [21]. The observed differences in their electrochemical properties suggest a strong dependence on crystal structure, underscoring the importance of identifying the most favorable polymorph for optimal cathode performance [21,22].

Computational and theoretical studies play a pivotal role in complementing experimental work by providing atomic-level insights into structural and electrochemical behavior. In this study, atomistic simulations employing classical interatomic potentials were used to investigate structural properties, point defect energetics, and sodium-ion migration pathways. This approach is well-suited for modeling structural defects, as it treats defects with their full formal charges. In contrast, the doping behavior of

isovalent and aliovalent elements was examined using density functional theory (DFT), a quantum mechanical framework capable of capturing essential electronic effects, such as defect-induced states, charge localization/delocalization, band gap variations, and Fermi level shifts that are critical for accurately assessing the impact of doping and intrinsic defects. These investigations aim to enhance understanding and guide the optimization of Na₂FeSiO₄ for improved performance in SIBs. Prior research has successfully employed atomistic simulations to investigate various electrode materials, demonstrating the value of this approach in advancing battery technology [23–34].

2 Computational methods

The General Utility Lattice Program (GULP), a classical simulation code, was employed to investigate the energetics of defects, dopants, and ionic diffusion in the system [35]. GULP is a versatile computational tool capable of modeling a wide range of materials including ionic solids, semiconductors, metals, and organic molecular crystals using classical force fields. Its functionalities include structure optimization, free energy minimization, molecular dynamics, defect analysis, force field fitting, and phonon free energy calculations [36]. Atomic interactions were modeled using a combination of long-range Coulombic forces and short-range interactions (Pauli repulsion and van der Waals attraction), with the latter represented by Buckingham potentials [37–39]. Structural optimizations were performed using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm, with convergence achieved when the gradient norm fell below 0.001 eV/Å [36].

Point defects and ion migration processes were modeled using the Mott–Littleton approach [40], which partitions the crystal into two regions: Region I (the inner zone), where atoms near the defect are explicitly relaxed using interatomic potentials, and Region II (the outer zone), where the response is treated using continuum or linear elastic approximations. Sodium-ion migration was studied by selecting two adjacent sodium lattice sites and defining seven equidistant interstitial positions along the diagonal connecting them. Ion hopping was evaluated along multiple directions (direct, *x*, *y*, *z*, *xy*, *xz*, and *yz*), and the corresponding defect formation energies were computed for each diffusion pathway. To minimize systematic errors, the midpoint between the selected sodium vacancy sites was used as the reference center for defect calculations. Activation energies for sodium-ion migration were calculated by treating the migrating ions as spherical particles with full ionic charges in the dilute limit. To account for polarization effects, the core–shell model was implemented, providing a more accurate

representation of ion–ion interactions.

To investigate the electronic properties of the doped configurations, DFT calculations were conducted using the Vienna *Ab initio* Simulation Package (VASP) [41]. The projected augmented wave (PAW) method was employed [42], with spin polarization enabled in all cases. Exchange–correlation interactions were treated using the generalized gradient approximation (GGA), specifically the Perdew–Burke–Ernzerhof (PBE) functional [43]. A plane-wave basis set with an energy cut-off of 500 eV was used for all simulations. Defect calculations were performed using a $2 \times 2 \times 2$ supercell comprising 128 atoms. For Brillouin zone sampling, a Monkhorst–Pack [44] k-point mesh of $4 \times 4 \times 4$ was applied for bulk $\text{Na}_2\text{FeSiO}_4$ optimization, while a reduced mesh of $2 \times 2 \times 2$ was used for defect modeling. Structural optimizations were considered converged when atomic forces were less than 0.001 eV/Å. To accurately capture the electronic structure of Fe, a Hubbard U correction was applied to the localized 3d orbitals, with $U = 4.00$ eV and $J = 0.00$ eV, in line with previous DFT studies [21]. Bader charge analysis [45] was conducted to estimate atomic charges and gain insight into the charge distribution within the system.

Table 1 Buckingham potential parameters [37–39] used in the classical simulations of two-body problems [$\Phi_{ij}(r_{ij}) = A_{ij} \exp(-r_{ij}/\rho_{ij}) - C_{ij}/r_{ij}^6$], where A , ρ , and C are parameters (The values of Y and K represent the shell charges and spring constants.)

Interaction	A/eV	$\rho/\text{\AA}$	$C/(\text{eV} \cdot \text{\AA}^6)$	Y/e	$K/(\text{eV} \cdot \text{\AA}^{-2})$
$\text{Na}^+ - \text{O}^{2-}$	1677.830	0.2934	0.00	1.0000	292.43
$\text{Fe}^{2+} - \text{O}^{2-}$	1105.2409	0.3106	0.00	2.0000	10.92
$\text{Si}^{4+} - \text{O}^{2-}$	1612.45920	0.29988	0.00	4.0000	9999
$\text{O}^{2-} - \text{O}^{2-}$	22764.0	0.149	27.88	−2.210	19.73

3 Results and discussion

3.1 $\text{Na}_2\text{FeSiO}_4$ crystal structure

$\text{Na}_2\text{FeSiO}_4$ is known to exhibit multiple polymorphic forms. Among these, the cubic, orthorhombic, and triclinic phases have been widely studied and are well-established in both experimental and theoretical literature. In contrast, the monoclinic phase has remained relatively underexplored. To address this gap, the present study focuses on a systematic investigation of the defect chemistry and sodium-ion diffusion behavior in the monoclinic structure.

The monoclinic structure of $\text{Na}_2\text{FeSiO}_4$ is classified under the $P1n1$ space group. Experimentally determined lattice parameters for this compound are $a = 7.19$ Å, $b = 5.65$ Å, and $c = 5.40$ Å, with angles $\alpha = \gamma = 90.00^\circ$ and $\beta = 89.96^\circ$, yielding a unit cell volume of 219.37 Å³ [46]. The structure features interconnected NaO_4 and SiO_4

tetrahedra through corner-sharing, forming a directional framework that supports a 3D Na-ion diffusion network (see Fig. 1(a)). The corner-sharing geometry of adjacent NaO_4 polyhedra largely facilitates this continuous diffusion pathway.

A comparison of the calculated and experimental lattice parameters for $\text{Na}_2\text{FeSiO}_4$ is presented in Table 2. The results show that the classical potential-based simulation closely replicates the experimental values, with minimal deviations. For instance, the calculated lattice parameter a (7.17 Å) differs by only 0.28% from the experimental value (7.19 Å), while b matches exactly (5.65 Å). The c parameter shows a slight deviation of 0.74%, and the monoclinic angle β (89.90°) closely aligns with the experimental value (89.96°), differing by just 0.06° . The calculated unit cell volume (220.4 Å³) is within 0.46% of the experimental volume (219.4 Å³). In contrast, DFT and DFT + U approaches tend to underestimate the lattice dimensions, especially along the a -axis, with deviations of 5.15% and 4.31%, respectively. These methods also yield larger discrepancies in unit cell volume, with errors of 4.96% for DFT and 4.33% for DFT + U. Overall, the classical interatomic potential demonstrates excellent agreement with experimental measurements, validating its reliability for modeling the structural properties of $\text{Na}_2\text{FeSiO}_4$.

The charge density distribution (Fig. 1(b)) reveals a significant accumulation of electronic charge around the oxygen atoms, consistent with their high electronegativity and key role in stabilizing the lattice. The density of states (DOSs), calculated using both standard DFT and DFT + U methods (Figs. 1(c) and 1(d)) show that the DFT + U approach results in a more localized description of the Fe 3d states, effectively opening the band gap and offering a more accurate representation of the electronic structure of $\text{Na}_2\text{FeSiO}_4$. This highlights the importance of applying Hubbard U corrections when modeling transition metal-containing systems to capture their true electronic behavior. Previous DFT simulation studies reported a band gap of approximately 1.23 eV for $\text{Na}_2\text{FeSiO}_4$ using lower U values [47], whereas the present study yields a band gap of around 3 eV, which aligns well with experimental values ranging from 2.58 to 2.87 eV [48].

Table 3 presents the results of the Bader charge analysis for atoms in bulk $\text{Na}_2\text{FeSiO}_4$. The Na atoms exhibit a charge of +1.00 |e|, indicating a nearly complete transfer of one electron, consistent with their expected +1 oxidation state. The Fe atom carries a Bader charge of +1.46 |e|, suggesting partial electron transfer and a degree of covalent character in its bonding, deviating from a fully ionic +2 or +3 state. Si shows a charge of +4.00 |e|, aligning well with its typical +4 oxidation state in silicate structures. The O atoms have a Bader charge of −1.86 |e|, close to the formal −2 charge value, indicating a high level of electron density retention.

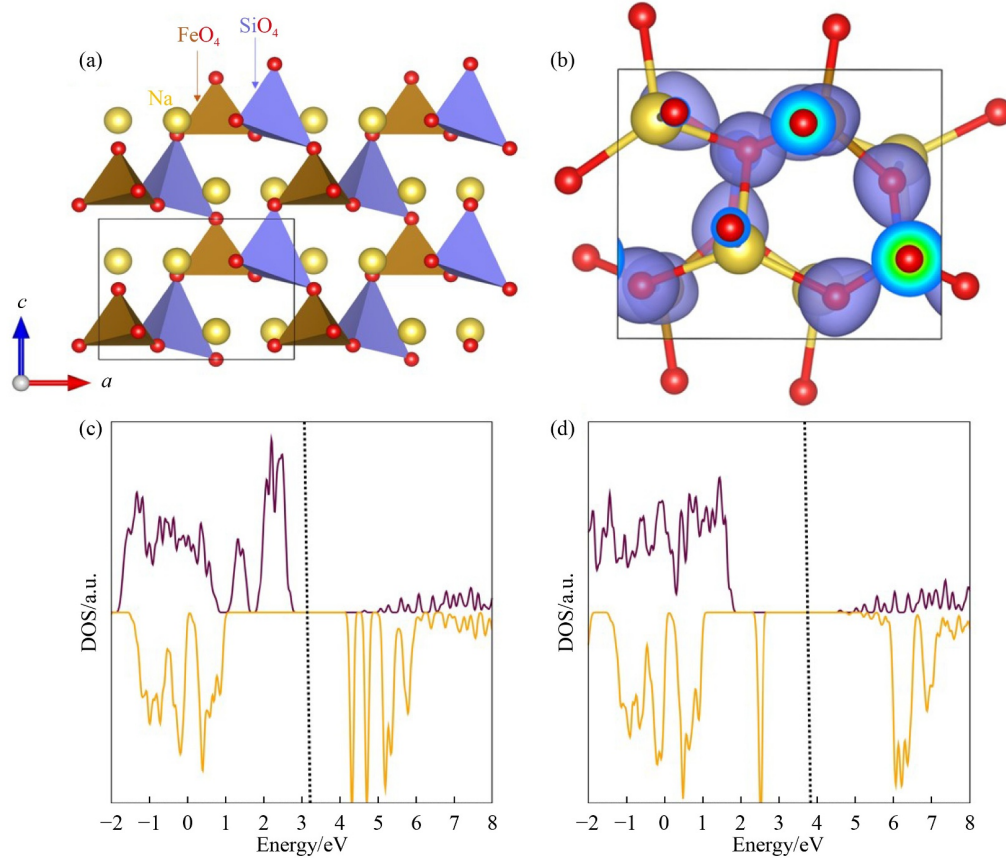


Fig. 1 Structural and electronic characteristics of $\text{Na}_2\text{FeSiO}_4$.

(a) Crystal structure of $\text{Na}_2\text{FeSiO}_4$ showing interconnected FeO_4 and SiO_4 tetrahedra with Na ions positioned in the framework; (b) charge density map illustrating electron accumulation around oxygen atoms; (c) electronic DOS calculated using standard DFT; (d) DOS obtained with the DFT + U method, highlighting the effects of on-site Coulomb correction.

Table 2 Comparison of calculated and experimental lattice parameters of $\text{Na}_2\text{FeSiO}_4$

Lattice parameters	Calculated			Experiment [46]	$ \Delta /\%$		
	Classical	DFT	DFT+U		Classical	DFT	DFT+U
$a/\text{\AA}$	7.17	6.82	6.88	7.19	0.28	5.15	4.31
$b/\text{\AA}$	5.65	5.68	5.68	5.65	0.00	0.53	0.53
$c/\text{\AA}$	5.44	5.38	5.37	5.40	0.74	0.37	0.56
$\alpha = \gamma/(\circ)$	90.0	90.0	90.0	90.0	0.00	0.00	0.00
$\beta/(\circ)$	89.90	89.25	89.56	89.96	0.06	0.79	0.44
$V/\text{\AA}^3$	220.4	208.5	209.9	219.4	0.46	4.96	4.33

Table 3 Bader charges on the atoms in the bulk $\text{Na}_2\text{FeSiO}_4$

Atom	Bader charge ($ e $)
Na	+1.00
Fe	+1.46
Si	+4.00
O	-1.86

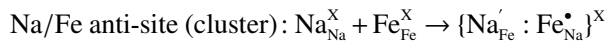
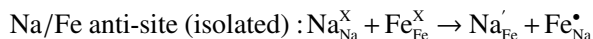
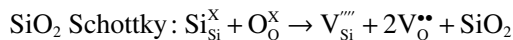
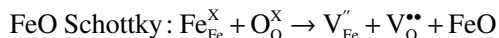
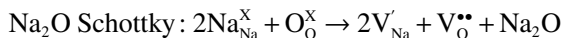
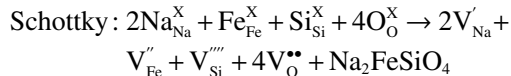
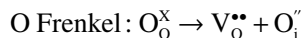
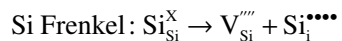
Overall, these results reflect the mixed ionic-covalent nature of bonding in $\text{Na}_2\text{FeSiO}_4$ and provide valuable

insights into the internal charge distribution within the crystal lattice.

3.2 Intrinsic defect processes in $\text{Na}_2\text{FeSiO}_4$

Intrinsic defects represent imperfections within the crystal lattice of a pure material, which can have a pronounced effect on its electrochemical performance and transport properties. In this study, particular focus was placed on point defects, including vacancies, interstitials, and anti-site defects. The formation energies of these defects were calculated and subsequently used to derive the Frenkel, Schottky, and anti-site defect formation energies by incorporating both lattice and point defect energetics. The formation energies of isolated and clustered anti-site defects were evaluated through cation exchange mechanisms, specifically considering the substitution of Na on Fe sites and Fe on Na sites, for both single and multiple exchange configurations. The intrinsic defect reactions are represented using the Kröger-Vink notation [49].





The calculated defect formation energies provide valuable insights into the thermodynamic stability of various intrinsic defects (see Fig. 2). Among the Frenkel defects, the Si Frenkel exhibits the highest formation energy (11.98 eV), while Na (1.71 eV), Fe (4.20 eV), and O (4.80 eV) Frenkel defects are energetically more favorable. The highest Frenkel energy calculated for Si corresponds to the formation of the most highly charged defect in the system. The overall trend in Frenkel defect energies follows the order of decreasing ionic charges ($\text{Si}^{4+} > \text{Fe}^{2+}$ or $\text{O}^{2-} > \text{Na}^{+}$). Lower Frenkel energies are associated with the relative ease of forming Na^{+} defects, which are essential for vacancy-mediated sodium ion migration.

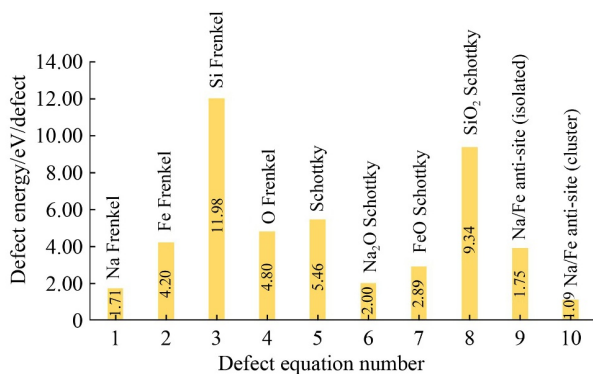


Fig. 2 Defect reaction energies.

Previous simulation studies using classical pair potentials have reported similar Na Frenkel defect energies in $\text{Na}_2\text{CoSiO}_4$ [50] and $\text{Na}_2\text{MnSiO}_4$ [51], with defect formation energy values around 1.60 eV per defect. Schottky defects display a wider range of formation energies, with Na_2O Schottky (2.00 eV) and FeO Schottky (2.89 eV) being more favorable compared to the general Schottky (5.46 eV) and SiO_2 Schottky (9.34 eV) defects.

Anti-site defects show relatively low formation energies, with isolated Na/Fe anti-site defects at 1.75 eV and clustered anti-site defects further stabilized at 1.09 eV, indicating a thermodynamic preference for defect clustering. The tendency to form anti-site defect clusters has also been observed in other Na-based silicate systems [50,51]. However, the formation of anti-site isolated defects (Na_{Fe}' and $\text{Fe}_{\text{Na}}^{\bullet}$) is more endothermic compared to both the Na Frenkel pair and the Na/Fe anti-site cluster, indicating a lower energetic favorability for individual defect formation.

While this study focuses on defect formation and sodium-ion diffusion based on static DFT calculations at 0 K, it is important to acknowledge that temperature plays a crucial role in real-world sodium-ion battery operation. Elevated temperatures can significantly influence defect dynamics, enhance ion mobility, and affect phase stability, particularly under repeated charge–discharge cycling conditions. Although temperature-dependent simulations such as *ab initio* molecular dynamics or phonon-assisted diffusion models were not included in this study, previous studies have shown that thermal effects can significantly alter ion migration barriers and defect equilibria in polyanionic frameworks [52,53].

3.3 Na-ion diffusion

Investigating Na-ion diffusion in electrode materials is crucial for identifying and optimizing candidates with favorable ionic conductivity. Experimental approaches to studying ion migration mechanisms and associated energy barriers often face challenges in resolving atomic-scale details due to inherent structural complexities and measurement limitations. In this study, atomistic simulations were conducted to explore potential Na-ion migration pathways and to calculate their corresponding activation energies. These computational insights enable the optimization of electrode performance by enhancing ionic conductivity, rate capability, and cycling stability, while also supporting experimental efforts and reducing development costs.

Four potential Na-ion hopping mechanisms associated with vacancy-mediated migration were identified, and their activation energies were calculated. The calculated activation energies for hops A and B are 0.41 and 0.38 eV, respectively, and these two hops establish a connected long-range diffusion pathway (see Figs. 3, 4(a) and 4(b)), with an overall activation energy of 0.41 eV. Hop C, which involves a relatively long Na–Na separation of 4.93 Å, is associated with a high activation energy of 2.27 eV (see Fig. 4(c)), occurring within the *ab* plane. The longest observed hopping distance is 5.79 Å, corresponding to an activation energy of 0.92 eV (see Fig. 4(d)). The extended diffusion pathway comprising hops C and D yields a total activation energy of 2.27 eV.

Due to this high energy barrier, such pathways are considered energetically unfavorable and are therefore excluded from further analysis. The energy profiles corresponding to these localized Na-ion hops are illustrated in the respective panels of Fig. 4.

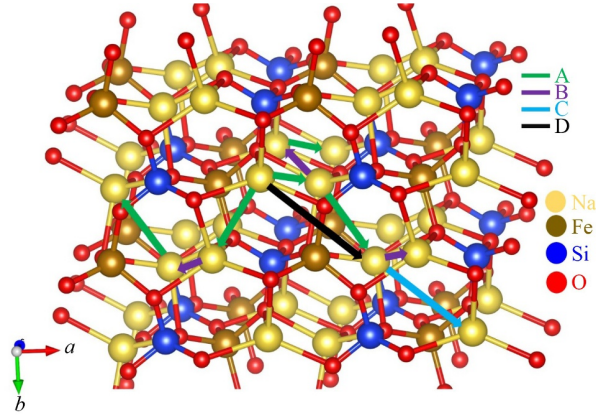


Fig. 3 Na-ion migration pathways in $\text{Na}_2\text{FeSiO}_4$.

The activation energy for Na-ion migration in $\text{Na}_2\text{FeSiO}_4$ is calculated to be 0.41 eV, which is moderate compared to other related silicate compounds. It is lower than that of $\text{Na}_2\text{MnSiO}_4$ (0.81 eV) [51] and also lower than several Li-based materials such as $\text{Li}_2\text{MnSiO}_4$ (0.54 eV) [54], $\text{Li}_2\text{FeSiO}_4$ (0.83 eV) [55], and $\text{Li}_2\text{CoSiO}_4$ (0.75 eV) [56], indicating relatively better ion mobility in $\text{Na}_2\text{FeSiO}_4$. However, $\text{Na}_2\text{FeSiO}_4$ has a higher activation

energy than $\text{Na}_2\text{CoSiO}_4$ (0.21 eV) [50], which exhibits the lowest migration barrier among the group.

These comparisons suggest that while $\text{Na}_2\text{FeSiO}_4$ does not provide the fastest ion transport, it achieves a favorable balance between ionic mobility and stability, making it a competitive candidate among Na-based silicates for energy storage applications, particularly where moderate ion transport and high thermal or electrochemical stability are required.

4 Solution of dopants

Doping in electrode materials involves the deliberate introduction of foreign atoms to alter the chemical composition, enhance structural integrity, and boost electrochemical performance. Doping is also a well-established strategy to modulate the properties of electrode materials, including their voltage profiles. Dopants can influence the redox behavior of transition metal centers by altering the electronic structure of the host material. Modifications to the DOS, band gap, and Fermi level position induced by dopants can shift the redox potentials of active species, thereby impacting the average operating voltage. Furthermore, dopants may stabilize certain oxidation states, suppress undesirable phase transitions, and improve the reversibility of sodium insertion/extraction processes. As a result, understanding the electronic effects of doping offers valuable insights

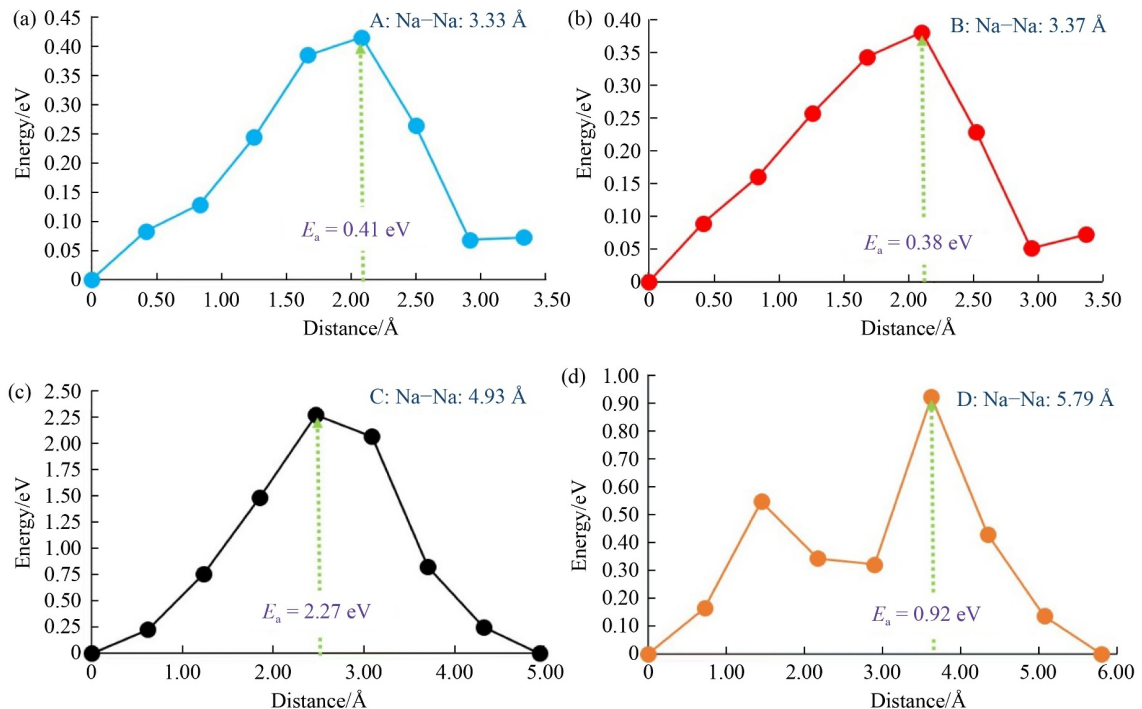


Fig. 4 Energy profile diagrams for the local Na hops with activation energies. Na-Na separation of (a) 3.33 Å; (b) 3.37 Å; (c) 3 Å; (d) 5.79 Å.

into voltage tuning and the overall electrochemical optimization of cathode materials.

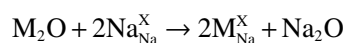
Dopants also play a vital role in accommodating structural distortions and alleviating internal stress during extended electrochemical cycling. By suppressing structural degradation and preventing unfavorable phase transitions during sodium-ion extraction and insertion, doping contributes significantly to improved cycling stability. It also helps minimize lattice volume fluctuations, widen ion diffusion pathways, and reinforce the overall structural framework, highlighting the importance of dopant engineering in the development of high-performance sodium-ion battery electrodes [57,58].

In particular, doping of Mn^{3+} plays a central role in the electrochemical behavior of cathode materials. During charge–discharge cycles, manganese undergoes redox transitions between these two valence states, directly influencing the capacity and voltage profile of the battery. However, the presence of Mn^{3+} is associated with Jahn–Teller distortion due to its high-spin d^4 electronic configuration. This distortion can lead to local lattice instabilities, phase transitions, and degradation of long-term cycling stability [59].

In this study, the solution energies of various isovalent and aliovalent dopants in $\text{Na}_2\text{FeSiO}_4$ were calculated to evaluate the energy required for their incorporation into the host crystal structure. Isovalent dopants have the same valence as the atoms they replace, maintaining charge neutrality, while aliovalent dopants possess a different valence, necessitating the formation of charge-compensating defects to preserve overall charge neutrality.

4.1 Monovalent dopants

Introducing monovalent dopants with a single positive charge at the Na sites in $\text{Na}_2\text{FeSiO}_4$ can play a crucial role in optimizing electrochemical performance and improving structural stability, highlighting the need for a detailed examination of viable doping strategies. In this study, the incorporation of monovalent dopants M^+ ($\text{M} = \text{Li}, \text{K}, \text{and Rb}$) at Na sites was investigated. The doping process is described by



The solution energy data for monovalent dopants in $\text{Na}_2\text{FeSiO}_4$, along with their respective atomic radii, reveal a significant size-dependent effect on dopant incorporation at Na^+ sites. Na^+ , with an ionic radius of 1.02 Å, serves as the reference ion for substitution. Among the dopants studied, Li^+ has a smaller radius (1.45 Å, though this value appears closer to its atomic radius rather than ionic), yet it exhibits the highest solution energy (1.00 eV). This suggests that, despite being smaller, Li^+ is not easily incorporated into the Na site, likely due to lattice distortion or electrostatic

mismatch. In contrast, K^+ (2.20 Å) and Rb^+ (2.35 Å) are significantly larger than Na^+ , yet they show much lower solution energies of 0.13 and 0.20 eV, respectively, indicating more energetically favorable incorporation.

This counterintuitive trend may arise from the ability of larger dopant ions to stabilize the surrounding structure by reducing local charge density or by occupying larger interstitial volumes in the host lattice. Additionally, the relatively low solution energies for K^+ and Rb^+ also suggest that the $\text{Na}_2\text{FeSiO}_4$ framework possesses sufficient structural flexibility to tolerate such size mismatches, possibly leading to enhanced structural robustness and the formation of wider Na-ion diffusion pathways.

Table 4 Solution energies of monovalent dopants substituted on the Na site

Dopants	Atomic radius/Å	Solution energy/eV
Li	1.45	1.00
K	2.20	0.13
Rb	2.35	0.20

Figure 5 illustrates the structural and electronic environment of K-doped $\text{Na}_2\text{FeSiO}_4$. The crystal structure confirms the successful incorporation of a K^+ ion (shown in purple) at a Na site, maintaining structural integrity without significant local distortion (Fig. 5(a)). Figure 5(b) presents the charge density difference plot, where the redistribution of electronic density around the K dopant and neighboring atoms confirms localized interactions without significant charge accumulation or depletion, suggesting that K^+ incorporation is electronically benign.

The total DOS plot (Fig. 5(c)) further supports this observation. The Fermi level remains positioned within the bandgap, characteristic of insulating behavior, and there is negligible contribution from the K dopant near the Fermi level, indicating that K doping does not introduce mid-gap states or significantly alter the electronic structure. The p-states of K lie deep in the valence band, far from the conduction and valence band edges (Fig. 5(d)). This confirms that K^+ can be incorporated with minimal electronic disruption, supporting its suitability as a dopant to enhance structural stability without compromising electronic properties.

4.2 Divalent dopants

A range of divalent dopants (Co^{2+} , Cu^{2+} , Zn^{2+} , Mn^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+}) was investigated for potential substitution at the Fe site. The thermodynamic viability of incorporating each dopant into the lattice was systematically assessed. The corresponding doping mechanism is described by

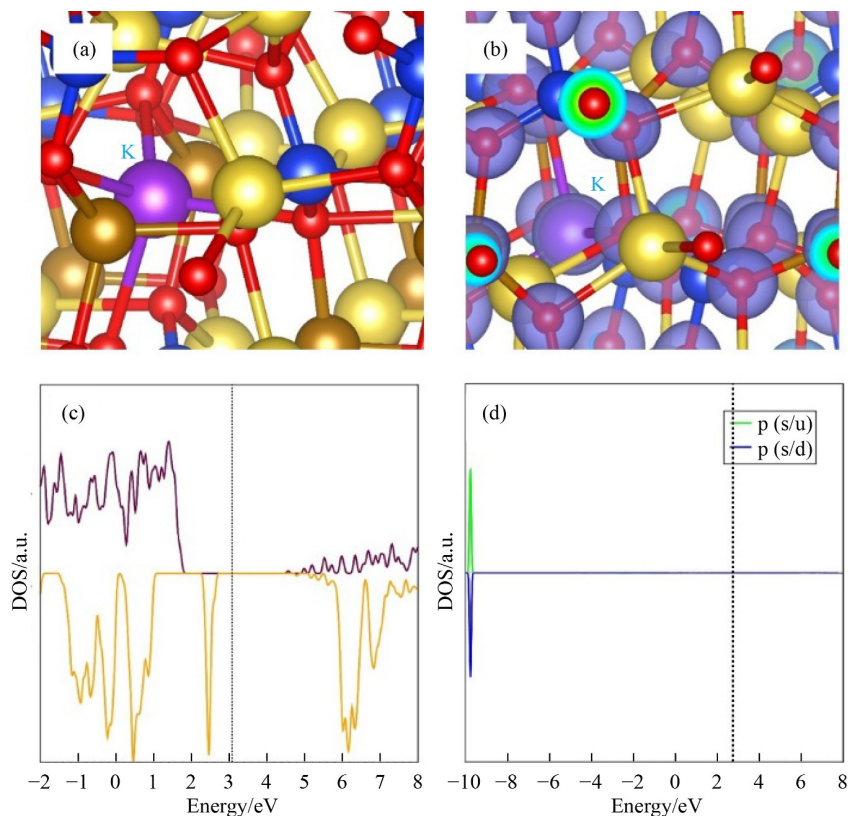
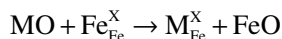


Fig. 5 Effects of K doping on Na₂FeSiO₄.

(a) Relaxed structure of K-doped Na₂FeSiO₄; (b) charge density plot associated with K-doping; (c) total DOS plot; (d) the atomic DOS plot of K.



The substitution of various divalent dopants at the Fe site in Na₂FeSiO₄ was analyzed by comparing their ionic radii and solution energies, with Fe²⁺ (0.78 Å) serving as the reference ion. Among the candidates, Zn²⁺ (0.74 Å), which closely matches the size of Fe²⁺, exhibited the lowest solution energy (0.47 eV), indicating highly favorable incorporation with minimal lattice distortion. Similarly, Mn²⁺ (0.82 Å) and Co²⁺ (0.58 Å) also showed moderate solution energies of 0.73 and 0.78 eV, respectively, suggesting they can effectively substitute for Fe²⁺ with minimal lattice distortion (see Table 5).

In contrast, Cu²⁺, despite its similar ionic radius

(0.73 Å), demonstrated a much higher solution energy of 1.74 eV, possibly due to unfavorable electronic interactions or the presence of Jahn–Teller distortion effects. Among the alkaline earth metal dopants, Ca²⁺ (1.00 Å) had a moderately low solution energy of 0.59 eV, indicating some potential for substitution. However, larger dopants such as Sr²⁺ (1.18 Å) and Ba²⁺ (1.35 Å) exhibited significantly higher solution energies, 1.85 and 2.41 eV, respectively, highlighting the increasing energetic penalty of incorporating oversized cations into the Fe site and the associated lattice strain.

Figure 6 illustrates the structural and electronic effects of Zn doping in Na₂FeSiO₄. Figure 6(a) shows the relaxed crystal structure with Zn incorporated at the Fe site, demonstrating that the overall structural integrity is preserved with minimal local distortion. The charge density difference plot in Fig. 6(b) reveals localized electronic redistribution around the Zn dopant and its neighboring atoms, indicating partial charge transfer and bonding interactions within the surrounding lattice. The total DOS depicted in Fig. 6(c) shows that the electronic structure near the Fermi level remains mostly unchanged, with the Fermi level positioned within the bandgap, confirming that Zn doping does not significantly alter the insulating nature of the host material. Figure 6(d), which presents the atomic-resolved DOS of Zn, shows that the

Table 5 Solution energies of divalent dopants substituted on the Fe site

Dopant	Ionic radius/Å	Solution energy/eV
Co	0.58	0.78
Cu	0.73	1.74
Zn	0.74	0.47
Mn	0.82	0.73
Ca	1.00	0.59
Sr	1.18	1.85
Ba	1.35	2.41

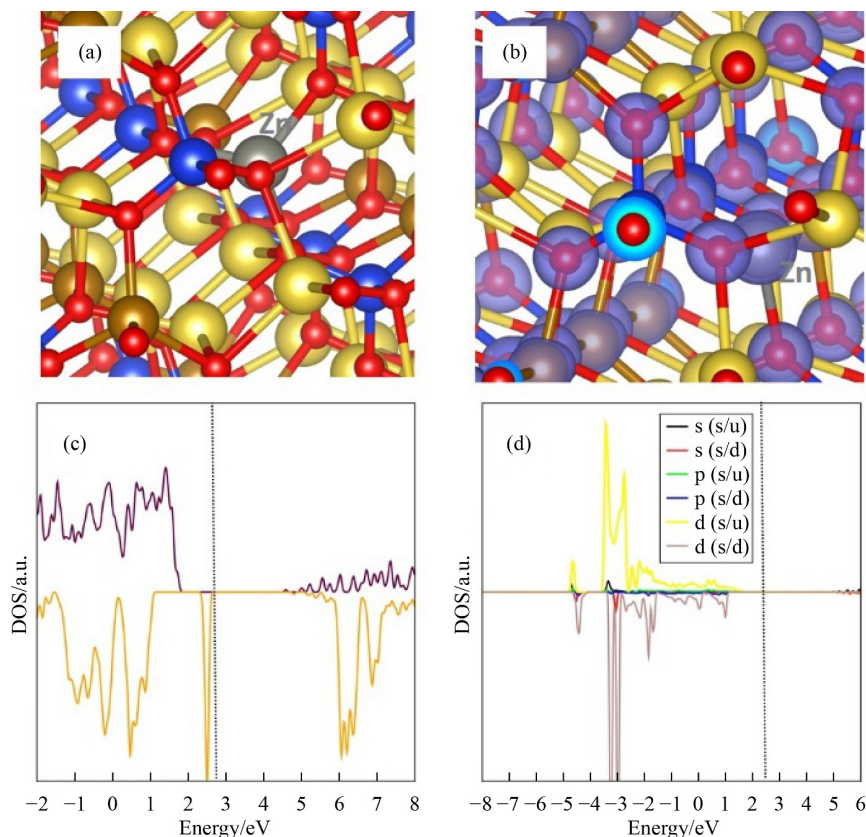


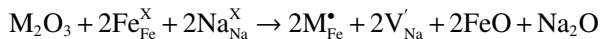
Fig. 6 Effects of Zn doping on $\text{Na}_2\text{FeSiO}_4$.

(a) Relaxed structure of Zn-doped $\text{Na}_2\text{FeSiO}_4$; (b) charge density plot associated with Zn-doping; (c) total DOS plot; (d) the atomic DOS plot of Zn.

Zn d-orbital states lie well below the Fermi level and do not introduce any mid-gap states, confirming that Zn incorporation is electronically benign and does not disrupt the host band structure.

4.3 Trivalent dopants

Introducing trivalent dopants at divalent Fe sites in $\text{Na}_2\text{FeSiO}_4$ induces the formation of sodium vacancies to maintain charge neutrality. These vacancies can promote vacancy-mediated Na-ion migration, thereby potentially enhancing the material's ionic conductivity. In this study, the effects of doping Al^{3+} , Ga^{3+} , Sc^{3+} , In^{3+} , and Y^{3+} at the Fe^{2+} site were explored. The corresponding doping mechanism can be expressed by



The solution energies of trivalent dopants substituted at the Fe^{2+} site in $\text{Na}_2\text{FeSiO}_4$ provide valuable insights into their incorporation behavior and thermodynamic feasibility. Among the dopants examined, Ga^{3+} (0.62 Å) exhibits the lowest solution energy of 3.78 eV, closely followed by Al^{3+} (0.54 Å) with 3.99 eV, indicating comparatively more favorable substitution among this group. These relatively small dopants cause less lattice

distortion, contributing to their lower incorporation energies. In contrast, larger dopants such as Sc^{3+} (0.75 Å), In^{3+} (0.80 Å), and Y^{3+} (0.90 Å) show progressively higher solution energies of 4.29, 4.33, and 4.70 eV, respectively. The increase in energy correlates with the increasing ionic radius, suggesting that size mismatch with the Fe^{2+} site (0.78 Å) leads to greater structural strain and reduced doping feasibility. While trivalent doping can enhance Na-ion mobility by inducing sodium vacancies, the high solution energies, particularly for larger dopants, highlight the need to balance ionic size compatibility with defect formation energetics for effective dopant selection.

Figure 7 shows the structural and electronic characteristics of Ga-doped $\text{Na}_2\text{FeSiO}_4$. In the relaxed

Table 6 Solution energies of trivalent dopants substituted on the Fe site

Dopant	Ionic radius/Å	Solution energy/eV
Al	0.54	3.99
Ga	0.62	3.78
Sc	0.75	4.29
In	0.80	4.33
Y	0.90	4.70

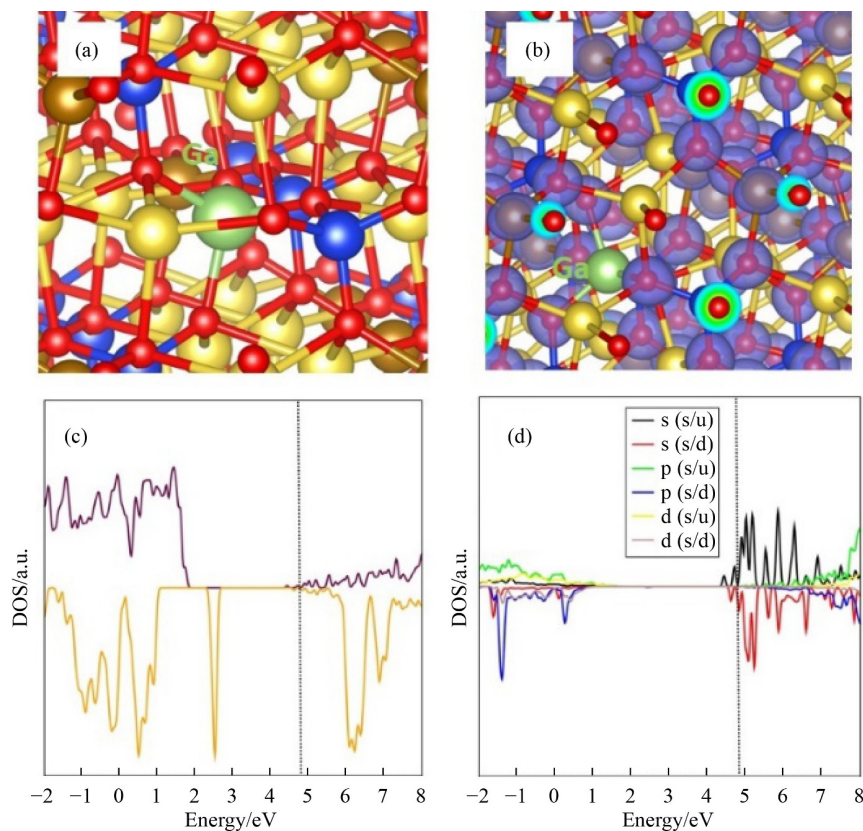


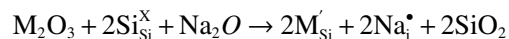
Fig. 7 Effects of Ga doping on Na₂FeSiO₄.

(a) Relaxed structure of Ga-doped Na₂FeSiO₄; (b) charge density plot associated with Ga-doping; (c) total DOS plot; (d) the atomic DOS plot of Ga.

atomic structure where a Ga³⁺ ion replaces the Fe²⁺ site, with minimal lattice distortion, indicating effective structural accommodation of the dopant (Fig. 7(a)). The corresponding charge density difference shows localized charge redistribution around the Ga atom and surrounding oxygen atoms, consistent with the formation of compensating defects such as Na vacancies to maintain charge neutrality (Fig. 7(b)). The total DOS plot (Fig. 7(c)) shows the Fermi level positioned within the bandgap, confirming that the material maintains its insulating nature after Ga incorporation. The atomic-resolved DOS plot for Ga reveals the contribution from s, p, and d orbitals of Ga primarily above the Fermi level, with no significant defect states appearing near or within the bandgap (Fig. 7(d)). This confirms that Ga doping does not introduce defect levels that would disrupt the electronic structure of the host.

Substituting trivalent dopants at the tetravalent Si sites introduces a net negative charge in the lattice. To preserve overall charge neutrality, an extra Na⁺ ion is inserted into an interstitial site for each dopant atom incorporated. This charge compensation mechanism not only stabilizes the crystal structure but also increases the overall sodium content, potentially enhancing the capacity of batteries utilizing this electrode material. In

this study, a range of trivalent dopants were explored for incorporation at the Si⁴⁺ site. The corresponding doping reaction is described by



The solution energies of trivalent dopants at the Si⁴⁺ site in Na₂FeSiO₄ reveal the challenges of substituting ions with significantly larger radii than the host cation. Given the small ionic radius of Si⁴⁺ (0.26 Å), all examined trivalent dopants, Al³⁺ (0.54 Å), Ga³⁺ (0.62 Å), Sc³⁺ (0.75 Å), In³⁺ (0.80 Å), and Y³⁺ (0.90 Å), are substantially larger (see Table 7). As a result, the solution energies are relatively high across the series, ranging from 5.71 eV for Al³⁺ up to 7.67 eV for Y³⁺. This clear trend of increasing solution energy with increasing ionic radius indicates that greater lattice distortion and higher energetic costs associated with incorporating larger ions at the Si site. Among the dopants, Al³⁺ and Ga³⁺ are the most favorable due to their smaller size and lower solution energies. Although doping at the Si site can potentially enhance capacity through the introduction of interstitial Na⁺ ions for charge compensation, the generally high solution energies, especially for larger dopants, highlight the structural constraints and limited feasibility of this doping pathway.

Table 7 Solution energies of trivalent dopants substituted on the Si site

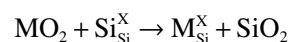
Dopant	Ionic radius/Å	Solution energy/eV
Al	0.54	5.71
Ga	0.62	5.74
Sc	0.75	6.73
In	0.80	6.94
Y	0.90	7.67

Figure 8 illustrates the structural and electronic effects of Al doping in $\text{Na}_2\text{FeSiO}_4$, where Al^{3+} substitutes for Si^{4+} . The relaxed configuration confirms successful incorporation of Al at the Si site with minimal local distortion, indicating effective structural compatibility (Fig. 8(a)). The charge density difference plot (Fig. 8(b)) reveals localized charge redistribution primarily around the Al atom and adjacent oxygen atoms. This redistribution reflects the introduction of an extra Na^+ ion at an interstitial site for charge compensation, in line with the trivalent-to-tetravalent substitution and charge compensation mechanism. The total DOS plot shows that the Fermi level remains within the bandgap, confirming

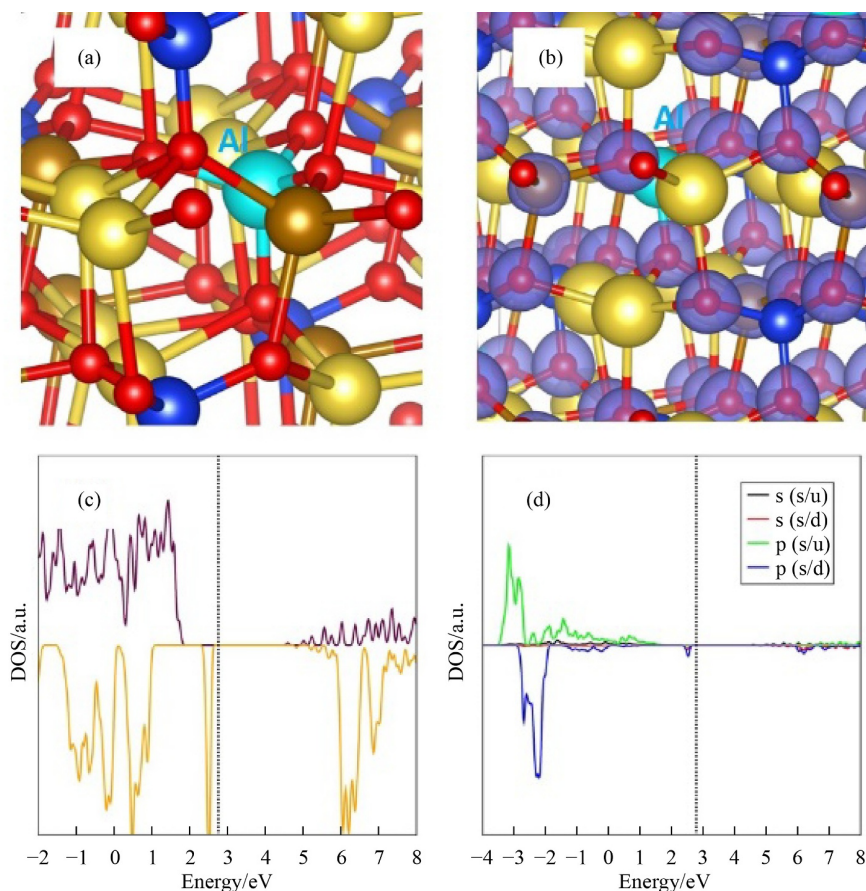
that Al doping preserves the insulating nature of the host material (Fig. 8(c)). The atomic-resolved DOS of Al (Fig. 8(d)) indicates that the Al p orbital states lie well below the Fermi level and no states are introduced within the bandgap. This suggests that Al incorporation is electronically benign, as it does not disrupt the electronic structure or introduce mid-gap states.

4.4 Tetravalent dopants

The substitution of tetravalent dopants at the Si site was examined to assess their impact on the structural stability and electrochemical performance. Dopants considered for replacing Si^{4+} included Ge^{4+} , Ti^{4+} , Sn^{4+} , Zr^{4+} , and Ce^{4+} . The corresponding doping mechanism is described by



The solution energies of tetravalent dopants at the Si^{4+} site indicate clear trends influenced by ionic size and lattice compatibility. Given the notably small ionic radius of Si^{4+} (0.26 Å), all considered dopants, Ge^{4+} (0.53 Å), Ti^{4+} (0.61 Å), Sn^{4+} (0.69 Å), Zr^{4+} (0.72 Å), and Ce^{4+} (0.87 Å), are significantly larger, leading to varying

**Fig. 8** Effects of Al doping on $\text{Na}_2\text{FeSiO}_4$.

(a) Relaxed structure of Al-doped $\text{Na}_2\text{FeSiO}_4$; (b) charge density plot associated with Al-doping; (c) total DOS plot; (d) atomic DOS plot of Al.

degrees of lattice distortion upon substitution. Among these, Ge^{4+} shows the lowest solution energy (2.05 eV), suggesting the highest structural compatibility and energetic favorability. Zr^{4+} (3.14 eV) and Sn^{4+} (3.87 eV) follow with moderate solution energies, indicating acceptable incorporation despite the size mismatch. Interestingly, Ti^{4+} , despite its relatively smaller radius (0.61 Å), displays a much higher solution energy (5.85 eV), possibly due to unfavorable local bonding or electronic interactions. Ce^{4+} , the largest dopant (0.87 Å), exhibits the highest solution energy (7.09 eV), reflecting substantial lattice strain and poor incorporation efficiency. These results underscore that, while all tetravalent dopants are larger than Si^{4+} , those with

moderately lower size mismatch, particularly Ge^{4+} , offer better structural compatibility and are more suitable for enhancing material performance through doping.

Figure 9 illustrates the effects of Ge doping on $\text{Na}_2\text{FeSiO}_4$. The relaxed atomic structure shown in Fig. 9(a) confirms preservation of the host lattice integrity upon Ge incorporation. The corresponding charge density distribution (Fig. 9(b)) reveals only minor charge redistribution around the Ge site, indicating limited bonding interaction with neighboring atoms. The total DOS (Fig. 9(c)) shows that Ge doping shifts the Fermi level closer to the valence band, which may enhance the electronic conductivity of the material. Further insight from the projected atomic DOS of Ge (Fig. 9(d)) reveals modest contributions from Ge 4p and 4d orbitals. These findings suggest that while Ge doping has a minimal impact on the local bonding environment, it can subtly modulate the electronic structure of $\text{Na}_2\text{FeSiO}_4$, potentially improving its electrochemical performance as a cathode material for SIBs.

Table 8 Solution energies of tetravalent dopants substituted on the Si site

Dopant	Ionic radius/Å	Solution energy/eV
Ge	0.53	2.05
Ti	0.61	5.85
Sn	0.69	3.87
Zr	0.72	3.14
Ce	0.87	7.09

4.5 Impact of dopants on the electronic properties

In many cases, the preservation of a wide band gap

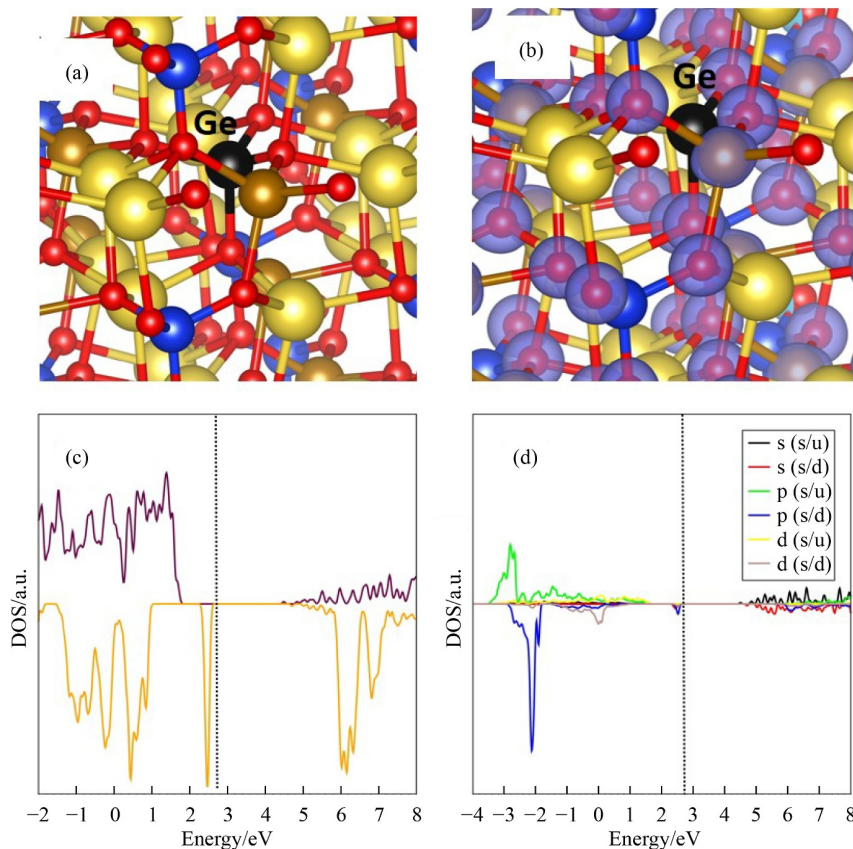


Fig. 9 Effects of Ge doping on $\text{Na}_2\text{FeSiO}_4$.

(a) Relaxed structure of Ge-doped $\text{Na}_2\text{FeSiO}_4$; (b) charge density plot associated with Ge-doping; (c) total DOS plot; (d) the atomic DOS plot of Ge.

suggests limited electron transport, which can restrict the rate capability and overall efficiency of the material, particularly at high current densities. To address this issue, several strategies can be considered, including surface carbon coating, incorporation of conductive additives like graphene or carbon nanotubes, or co-doping with elements known to introduce shallow donor or acceptor levels [60,61]. These approaches could enhance electronic conductivity without compromising structural integrity, thereby improving the practical applicability of doped $\text{Na}_2\text{FeSiO}_4$ as a cathode material for SIBs.

5 Conclusions

In conclusion, atomistic simulations were employed to explore the energetics of intrinsic point defect formation, Na-ion migration pathways, and dopant incorporation in $\text{Na}_2\text{FeSiO}_4$, providing valuable insights into its viability as a cathode material for SIBs. Among the native defects, the Na Frenkel pair exhibited the lowest formation energy, suggesting a natural preference for vacancy-mediated Na-ion migration. The calculated migration energy barriers of 0.38 and 0.41 eV further confirm the material's capability for efficient sodium-ion transport. Doping analysis identified K, Zn, and Ge as the most favorable isovalent dopants at the Na, Fe, and Si sites, respectively, while Ga showed a strong preference for substitution at Fe sites, facilitating Na-vacancy formation. Additionally, Al substitution at the Si site was found to increase the overall sodium content in the lattice. The electronic structures of these promising dopants were further investigated using DFT, offering deeper understanding of their influence on the electrochemical behavior of $\text{Na}_2\text{FeSiO}_4$. Future work should prioritize experimental validation of these computational findings and explore co-doping strategies, temperature-dependent defect dynamics, and long-term cycling behavior to further optimize $\text{Na}_2\text{FeSiO}_4$ for practical sodium-ion battery applications.

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Competing Interests The authors declare that they have no competing interests.

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