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ABSTRACT

There is intensive research by the community to improve materials for energy storage applications beyond lithium-ion batteries. The use of sodium as the charge carrier has benefits and can revolutionize the field. The wide use of sodium-ion batteries is partially hindered by the slow diffusion of sodium ions in the anode. Here, we use density functional calculations to investigate the diffusion properties of sodium ions in $Na_2Ti_3O_7$. We introduce trivalent [aluminum (Al), gallium, and scandium] and tetravalent (silicon, germanium, and tin) substitutional dopants to calculate their impact on the Na self-diffusion process. Considering a potential migration pathway, sodium atoms migrate via the vacancy mechanism with an energy barrier of 0.69 eV in undoped $Na_2Ti_3O_7$. This is substantially reduced by 0.3 eV when an Al atom substitutes for a titanium atom in the pathway of migration.

INTRODUCTION

The use of lithium-based batteries has become ubiquitous for the majority of portable electronic devices and is also the most widely used renewable energy storage. Nevertheless, the growing demand for lithium, coupled with its limited supply, high extraction costs, and environmental impact, has motivated the quest for alternative technologies that can offer similar performance, with less environmental impact and at a lower cost.

Sodium, unlike lithium, is abundantly available and widely distributed across the globe, making it a more cost-effective and sustainable resource. It is anticipated that sodium-based batteries will gain in importance and emerge in the near future as a promising contender for energy storage. Sodium-ion batteries (SIBs), specifically, operate on similar principles to their lithium counterparts but with the sodium ions as charge carriers, potentially reducing the environmental and economic impacts associated with lithium mining and processing.

The most common types of anode materials for SIBs are carbon-based, and specifically, hard carbon has been favorable since it has shown good intercalation, capacity, and capacity retention.[1] The problem, however, is the formation of sodium dendrite as a result of a very low voltage plateau, which is a major issue for potential commercial use. The recent report by Senguttuvan *et al.*[2] showed that sodium titanate ($Na_2Ti_3O_7$) can be reversibly intercalated by sodium with a plateau centered at 0.3 V. A plateau with this voltage can be quite advantageous in a full cell with a suitable cathode in terms of the energy density, in comparison to other studied materials, such as $Na_3V_2(PO_4)_3$ (1.6 V),[3] Na_XVO_2 (1.75 V),[4,5] Ni_3S_2 (0.94 V),[6] or $NaTi_2(PO_4)_3$ (2.1 V),[7] as well as carbon anodes.

In previous density functional theory (DFT) studies, there is a range of $Na_2Ti_3O_7$ bandgaps that were reported, ranging from 3.10 to 3.7 eV.[8–11] In a recent study, Irranious *et al.*[12] investigated the intrinsic defect process of the related monoclinic phase (P2/m space group) of $Na_2Ti_3O_7$ using atomistic simulations and showed that the Na ions have the lowest Frenkel energy. Importantly, they calculated using classical potential static atomistic simulation techniques that the activation migration energy for Na ions via the vacancy mechanism in the ab-plane is only 0.23 eV.[12] This, in turn, constitutes $Na_2Ti_3O_7$, an important candidate anode material for Na-ion batteries.

In the present study, we consider the structural, dynamic, and electronic properties of $Na_2Ti_3O_7$ (monoclinic, $P2_1/m$ space group) as they are related to its potential application as an anode material for solid state sodium-ion batteries. We employ DFT calculations to calculate the migration energy barriers and the impact of selected dopants in $Na_2Ti_3O_7$.

METHODOLOGY

The Vienna *Ab initio* Simulation Package (VASP) was employed to perform DFT calculations[13] using the Generalized Gradient Approximation (GGA) as parameterized by the PBESol (Perdew, Burke, and Ernzerhof for solids) functional,[14] which is an efficient way to model crystalline solids. In all cases of convergence testing and ion diffusion studies, there was full atomic and volume relaxation. The cut-off energy that met the convergence criteria is 550 eV. A 3 × 2 × 1 Monkhorst–Pack[15] mesh (0.04 k-spacing) and a 1 × 3 × 2 supercell with 144 atomic sites were used for all the calculations. The minimum energy pathway of Na diffusion was calculated under these conditions by the use of the Climbing Image Nudged Elastic Band (CI-NEB) method.[16]

RESULTS AND DISCUSSION

Structural properties

Experimental studies[17–19] confirmed that $Na_2Ti_3O_7$ is monoclinic, belonging to the $P2_1/m$ space group. They elucidated that the bulk structure consists of $(Ti_3O_7)^{2-}$ layers that are held together by sodium ions, which occur at two different crystallographic sites. The three independent Ti atoms have six anions at nearest neighbor sites, forming strongly distorted octahedra sharing their edges, which are the building blocks of the crystal structure. A schematic representation of the crystal structure is given in Fig. 1.

In Table I, we report the predicted DFT lattice parameters of the present study as compared to those determined in previous experimental investigations.[18,19] The deviations of the predicted values from the experimental ones are small (less than 1.14%), indicating that the computational parameters are well converged and appropriate for the system.

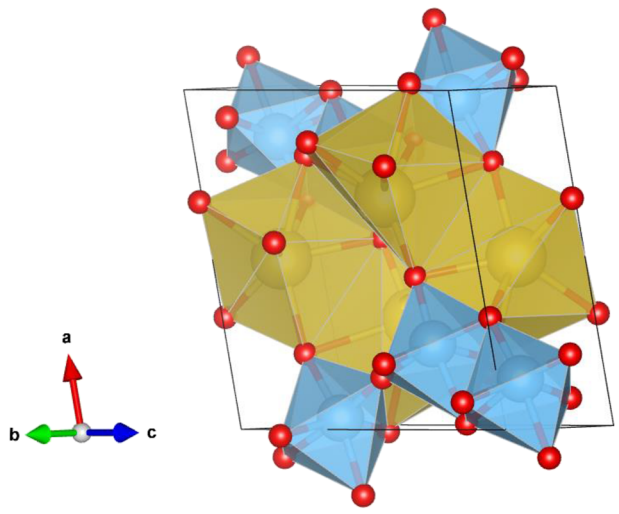

FIG. 1. Crystal structure of $Na_2Ti_3O_7$.

TABLE I. Predicted lattice parameters as compared to previous experimental studies.[18,19]

(Å)	Present (DFT)	Silva *et al.* (XRD)	Yakubovich *et al.*	Deviation silva (XRD) (%)	Deviation Yakubovich (%)
a	9.232	9.128	9.133	1.14	1.09
b	3.835	3.802	3.806	0.87	0.77
c	8.606	8.563	8.566	0.50	0.46

Doping strategies

Doping energy materials can improve their physical, mechanical, and electronic properties.[20–25] There are numerous important sodium containing materials being considered for battery applications, including $Na_3V(PO_4)_3$, $Na_2Ti_3O_7$, $NaZr_2(PO_4)_3$, $Na_3Fe_2(PO_4)_3$, $Na_2MnP_2O_7$, and $Na_2FeP_2O_7$.[26–30] For sodium-ion batteries to become competitive with lithium-ion batteries, the energetics of sodium self-diffusion must be competitive as they influence the charge/discharge rates and the energy density of the cells.

Typically, in oxide materials, dopant atoms are introduced as substitutionals in cation sites. In oxides, the introduction of dopants can be used to defect engineer the properties of the host material but also equally importantly to increase the concentration of the diffusing species or the concentration of the intrinsic point defects (i.e., typically vacancies or self-interstitials).

The introduction of trivalent atoms (M = Al, Ga, and Sc) in $Na_2Ti_3O_7$ takes place via the following relation (in the Kröger–Vink notation):

$$M_2O_3 + 2Ti_{Ti}^{x} + Na_2O \rightarrow 2M'_{Ti} + 2Na_i^{\cdot} + 2TiO_2, \quad (1)$$

where M'_{Ti} is a trivalent atom substitutional at the Ti site. This has an effective single negative charge as denoted by $'$, and $Na_i^{\cdot}$ denotes a sodium interstitial atom with an effective single positive charge as denoted by the dot. The $Na_i^{\cdot}$ charge balances M'_{Ti}. In essence, by introducing the trivalent atoms in the material, we can simultaneously increase the concentration of $Na_i^{\cdot}$.

In the static atomistic simulation study by Irranious *et al.*,[12] it was shown that energy is required for the solution of M_2O_3 for M = Al, Ga, and Sc, with the smaller dopant (Al) having the lowest solution energy. This, in turn, was justified by Al having the nearest ionic radius to Ti in the six-coordinated environment that is accommodated in the $Na_2Ti_3O_7$ lattice.[12]

It is feasible in this system to introduce tetravalent dopants (*R* = Si, Ge, and Sn),

$$RO_2 + Ti_{Ti}^{x} \rightarrow R_{Ti}^{x} + TiO_2, \quad (2)$$

where R_{Ti}^{x} is a tetravalent atom substitutional at the Ti site. From this relation, it is shown that as the tetravalent dopants are isovalent to the Ti atoms they substitute, there is no requirement for the formation of other defects to charge balance the incorporation. This

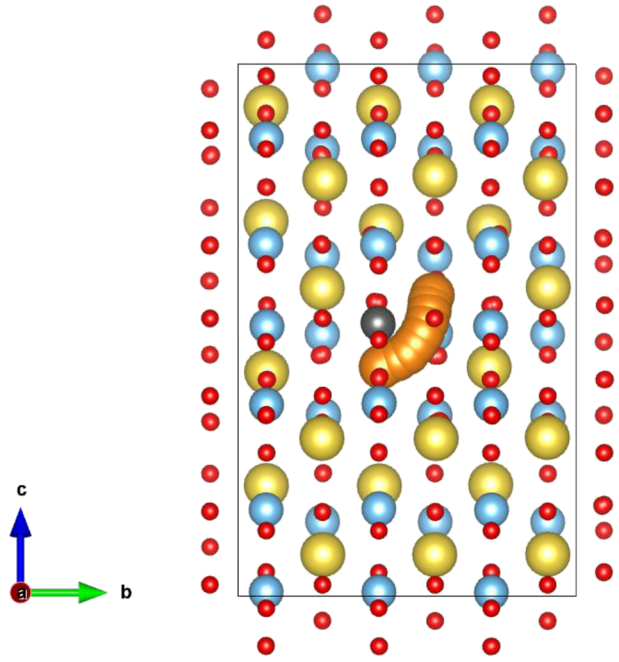

FIG. 2. The diffusion pathway (orange) of the sodium vacancy in doped $Na_2Ti_3O_7$. The black sphere corresponds to the dopant substitutional atom.

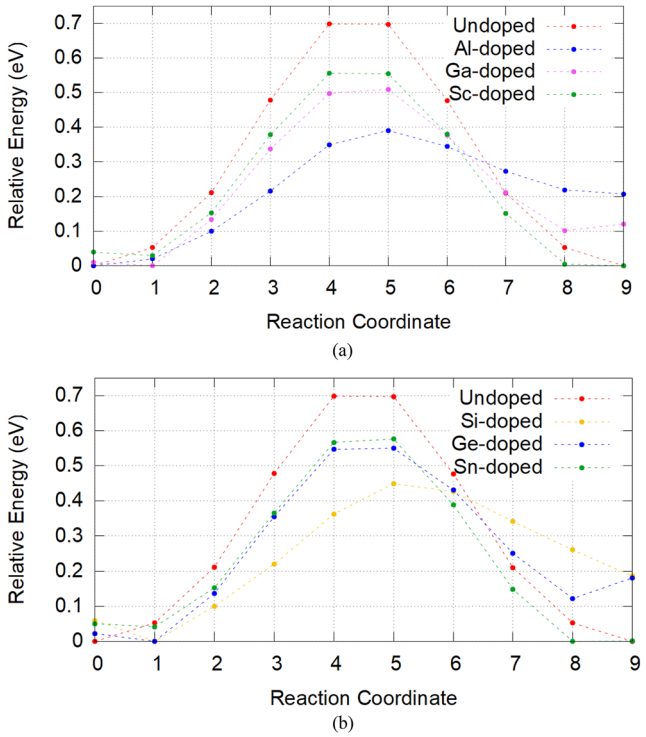

FIG. 3. Sodium self-diffusion migration energy profiles with respect to distance for the undoped material with the presence of (a) a trivalent and (b) a tetravalent dopant.

is different from the case of the trivalent dopants where the formation of $Na_i^{\cdot}$ is required. Considering the solution energies of Ge and Sn, Irranious *et al.*[12] calculated that they are negative. This, in turn, implies that Ge and Sn can readily be incorporated in the $Na_2Ti_3O_7$ lattice. The introduction would be beneficial only if they reduced the migration energy barriers of sodium ions.

Migration energy barriers

We first considered the migration energy of sodium diffusing via the vacancy mechanism along a typical pathway in $Na_2Ti_3O_7$. We calculated the migration energy for this path to be 0.69 eV, in good agreement with the 0.23–0.76 eV result by Irranious *et al.*[12] in the related phase of $Na_2Ti_3O_7$. The difference can be attributed to the use of NEB/DFT here as opposed to the previous static atomistic simulation study,[12] and these discrepancies have been discussed in previous studies considering oxide materials.[31] The impact of dopants on the sodium self-diffusion in this material has not been determined. In Fig. 2, we present a typical diffusion pathway of the sodium vacancy in doped $Na_2Ti_3O_7$. The migration energy profiles are shown in Fig. 3. It can be observed that the introduction of Al has the most significant effect and reduces the migration energy barrier of sodium by 0.3 eV as compared to the undoped case. Interestingly, all the dopants decrease the migration energy barrier of sodium self-diffusion (refer to Fig. 4). To summarize the results, Table II reports the calculated migration energy barriers for sodium self-diffusion in doped $Na_2Ti_3O_7$ as compared to the sodium migration energy

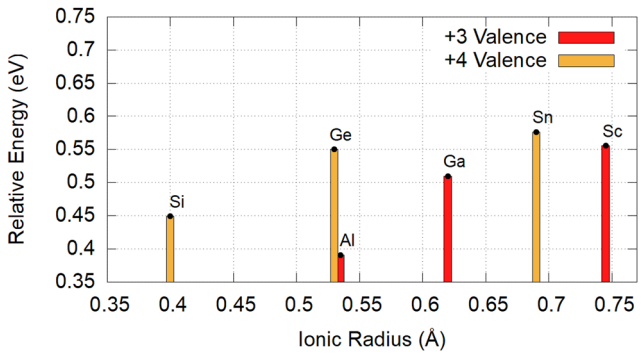

FIG. 4. Comparison of the migration energy barriers with respect to the ionic radius of the dopant in $Na_2Ti_3O_7$.

TABLE II. Predicted migration energy barriers for sodium self-diffusion in doped $Na_2Ti_3O_7$. The final column indicates the reduction from the 0.69 eV sodium migration energy barrier in undoped $Na_2Ti_3O_7$.

Dopant	Migration energy (eV)	Difference to undoped (eV)
Al	0.39	0.30
Ga	0.51	0.18
Sc	0.56	0.13
Si	0.45	0.24
Ge	0.55	0.14
Sn	0.58	0.11

barrier in undoped $Na_2Ti_3O_7$. Considering the tetravalent dopant Si (the smallest tetravalent dopant considered), it has the most impact, reducing the migration energy barrier by 0.24 eV.

CONCLUSIONS

In the present study, we have employed DFT calculations to investigate the Na self-diffusion properties in doped $Na_2Ti_3O_7$, which is a candidate anode material for solid state sodium-ion batteries. We consider a potential migration pathway, where sodium atoms migrate via the vacancy mechanism, and calculate an energy barrier of 0.69 eV in undoped $Na_2Ti_3O_7$. This is in good agreement with previous studies. Thereafter, we introduced the trivalent (Al, Ga, and Sc) and tetravalent (Si, Ge, and Sn) substitutional dopants to calculate their impact on the Na self-diffusion process. It is calculated that all the dopants considered lower the migration energy of Na self-diffusion. Therefore, they have a beneficial impact on the material for its application as a solid-state sodium-ion battery. In that respect, the doping with Al lowers the migration energy barrier of sodium the most (by 0.3 eV). Trivalent atoms will increase the number of sodium interstitials that can be incorporated in the lattice, and this needs to be determined experimentally whether it will be beneficial. Considering tetravalent dopants, they do lower the migration energy of sodium but to a lesser extent. The highest reduction is due to silicon, which is the smallest tetravalent dopant considered. Experimental work will be required to determine the solubility limits of these tetravalent atoms and whether they can be readily incorporated in the lattice.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Vasileios Balaouras: Data curation (equal); Investigation (equal); Writing – original draft (equal). **Nikolaos Kelaidis**: Data curation (equal); Investigation (equal); Writing – original draft (equal). **Alexander Chroneos**: Formal analysis (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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