First-Principles Investigations on Sodium Superionic Conductor Na$_{11}$Sn$_2$PS$_{12}$

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Supporting Information

ABSTRACT: Sodium superionic conductors are key components of solid-state sodium ion batteries, which are regarded as promising alternative energy storage options for large-scale application. Recently, a new crystalline sodium superionic conductor Na$_{11}$Sn$_2$PS$_{12}$ was reported with a remarkably high ionic conductivity over 1 mS/cm at room temperature. Herein, we report the comprehensive first-principles investigations on this new sodium superionic conductor. Our ab initio molecular dynamics simulations confirm the intrinsically fast and isotropic diffusion of sodium ions in Na$_{11}$Sn$_2$PS$_{12}$ involving all the sodium sites. From a series of first-principles calculations, we propose a sodium diffusion mechanism and discuss the effects of various defects or substitutions on the diffusion kinetics, which may aid in further development of this class of materials. Moreover, we argue that the inherent vacant sites (Wycko position 8b), whose presence has been claimed to be critical for the fast sodium diffusion in this material, are less likely to contribute to the sodium diffusion. Finally, the thermodynamic stability and chemical compatibility of Na$_{11}$Sn$_2$PS$_{12}$ are comparatively explored. Our theoretical study provides a more comprehensive understanding of Na$_{11}$Sn$_2$PS$_{12}$-type conductors as well as helpful guidance on their optimal design for application in solid-state batteries.

INTRODUCTION

Sodium-ion batteries have received much attention as an alternative to lithium-ion batteries for large-scale applications, because of the global availability and low cost of sodium resources relative to those of lithium. Recently, solid-state sodium ion batteries, which use a solid electrolyte, are being considered as feasible options in terms of cost and safety, since the use of flammable organic electrolytes in conventional sodium-ion batteries is one of the concerns that may become important with respect to safety, especially for large-scale applications. While much research has been reported on lithium superionic conductors in recent years for all solid-state lithium ion batteries, the development of sodium ion conductors has been less actively sought after. For the practical use of solid-state batteries, highly conductive solid electrolytes with ionic conductivities comparable to that of a liquid electrolyte (>1 mS/cm at room temperature) are indispensable. Traditionally, oxides-based sodium conductors have been extensively studied including β'-alumina and sodium (Na) superionic conductor (NASICON)-type conductors, which are reputed to exhibit ionic conductivities over 1 mS/cm at room temperature. Nevertheless, rigorous heat-treatment conditions for the synthesis and the technical difficulties in controlling the grain-boundary and interfacial resistance for the oxide-based materials are challenging issues to be resolved, which have retarded their applications in solid-state batteries.

Sulphide-based sodium superionic conductors have been lately highlighted with their high ionic conductivity and the mechanical properties that enable easy fabrication using simple cold pressing, and in part due to the success of the sulphide-based lithium superionic conductors. Na$_3$PS$_4$, Na$_{10}$M$_2$PS$_{12}$ (M = Si, Ge, Sn), and Na$_7$P$_3$S$_{11}$ have been reported experimentally or computationally, exhibiting promising electrochemical performances. Reported with an ionic conductivity of over 0.1 mS/cm at room temperature, Na$_3$PS$_4$-type conductors have been the intensively studied, and various compositional tuning methods, such as aliovalent doping of P$_5^+$ with Si$_{4+}$ or S$_{2-}$ or Cl$^-$/I$^-$_$22,23$ and isovalent substitution of S$_5^+$ with As$_{5+}$/Sb$_{5+}$ or S$^2-$ with Se$_{2-}$,$^{29-31}$ have been applied to achieve higher conductivity.$^{20-23}$ Simultaneously, a series of computational studies has been carried out to elucidate the fast sodium kinetics of Na$_3$PS$_4$-type conductors, with respect to the crystal symmetry and defect concentrations such as sodium vacancy of interstitial.$^{32-35}$

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Another important milestone for sulfide-based sodium superionic conductors was achieved more recently.\textsuperscript{36–40} Zhang et al.\textsuperscript{36} and Duchardt et al.,\textsuperscript{37} independently, introduced the Na$_{11}$Sn$_2$PS$_{12}$ phase with the highest sodium ionic conductivity reported to date for sulfide-based materials. It was demonstrated that Na$_{11}$Sn$_2$PS$_{12}$ is capable of delivering an ionic conductivity of 1.4 mS/cm with an activation energy of 0.25 eV\textsuperscript{36} or 3.7 mS/cm with an activation energy of 0.387 eV\textsuperscript{37} at room temperature. Zhang et al. proposed that the occurrence of quasi-isotropic diffusion is the origin of the high ionic conductivity, which involves equi-energetic sodium sites in the structure.\textsuperscript{36} On the other hand, Duchardt et al. suggested that the structural aspect containing a relatively large vacant space (Wyckoff position 8b) does not govern the overall ionic conductivity.\textsuperscript{38} They claimed that, from a comparative study with an Sb analogue (Na$_{11}$Sn$_2$Sb$_2$S$_6$), the major sodium diffusion did not take place through these 8b vacant sites. And, it was suggested that the 8b vacant site involving those vacant sites (Wyckoff position 8b) does not govern the ionic conductivity.\textsuperscript{38} Thus, the presence of the vacant sites and the local hopping through the sites were regarded as the key prerequisites for the fast diffusion, referred to as vacancy-controlled Na$^+$ superion conduction.\textsuperscript{39} However, the role of the vacant sites (8b) in the structure remains controversial and currently under debate. In a more recent report by Ramos et al., it was speculated that sodium diffusion did not take place through these 8b vacant sites.\textsuperscript{36}–\textsuperscript{38} The initial velocities of the ions were designated according to the Boltzmann distribution at 100 K, and the samples were heated to elevated temperatures using velocity scaling. After an equilibrium step of longer than 10 ps, data sampling was performed until the diffusivity converged (40–100 ps) in the canonical (NVT) ensemble with a Nose–Hoover thermostat.\textsuperscript{50,51} The sodium ionic conductivity $\sigma$ was derived from the Nernst–Einstein equation:

$$\sigma(T) = \frac{\rho^2 F^2 D(T)}{RT}$$

(1) where $\rho$, $z$, $F$, $R$, and $T$ are the molar density of sodium ions, the charge of a sodium ion, Faraday constant, gas constant, and temperature, respectively. The diffusivity, $D$, was calculated from a linear fitting as\textsuperscript{42,49,52}

$$D = \frac{1}{2d^2} \left( \langle \Delta r(t)^2 \rangle \right)$$

(2) where $d$ is the dimension of diffusion, $t$ is time, and $\langle \Delta r(t)^2 \rangle$ is the mean square displacement of sodium ions. The probability density, $p$, a time-averaged value of sodium ions on a three-dimensional grid, was calculated by counting the number of sodium ions at each grid point and averaging the values over the simulation time.\textsuperscript{53} To construct the structures with a sodium vacancy/interstitial, one sodium ion was removed from or added to the supercell of Na$_{10}$Sn$_{19}$P$_2$S$_{39}$, while the lattice parameters were fixed to those of the pristine structure to evaluate the effects independently. The lattice parameters were not significantly altered even when the full relaxation of the structure was carried out.

### Constructing Phase Diagrams.

Relevant phase diagrams were constructed using all the stable phases (Table S1) in the Na–Sn–P–S–Ti chemical space of the Materials Project database.\textsuperscript{52–55} We recalculated the stable phases using the calculation conditions described in First-Principles Energy Calculation. The energy correction for sulfur was applied, as adopted in the Materials Project database.\textsuperscript{53,54} To examine the intrinsic electrochemical stability, a sodium grand potential phase diagram was constructed by opening the system to a sodium reservoir with a chemical potential of sodium,\textsuperscript{55} which can be expressed as

$$\mu_{Na}(U) = \mu_{Na}^{0} - eU$$

(3) where $\mu_{Na}$ is the chemical potential of sodium, $\mu_{Na}^{0}$ is the elemental chemical potential of sodium, $U$ is the applied potential reference to sodium metal. The grand potential $\Phi$, the characteristic thermodynamic potential in the grand canonical ensemble, can be defined as

$$\Phi(c, U) = E(c) - n_{Na}(c) \mu_{Na}(U)$$

(4) where $E(c)$ is the internal energy of the structure and $n_{Na}(c)$ is the number of sodium atoms in the structure with composition c. Then,
the reaction energies of the intrinsic electrochemical decomposition 

\[ E_{\text{electrode}}(U) = \Delta \Phi(\epsilon_{SE}, U) = \sum_{i} E(\epsilon_{i}) - E(\epsilon_{SE}) - \Delta E_{\text{decomp}}(U) \]

where \( \epsilon_{SE} \) is the composition of the solid electrolyte, \( \sum E(\epsilon_{i}) \) is the sum of the internal energies of the decomposed phases, and \( \Delta E_{\text{decomp}} \) is the change in the number of sodium atoms after the reaction. To investigate the interfacial compatibility between the electrodes and electrolyte, the interfaces were regarded as pseudobinary phase diagrams, and potential mutual decomposition reactions were examined.\(^58,59\) The pseudobinary phase diagrams were extracted from the multitemporal phase diagrams by taking the compositions of the electrode and electrolyte to each end point. The reaction energies of mutual decomposition at the interface \( E_{\text{decomp}}(x) \) were determined using the following equation:

\[ E_{\text{decomp}}(x) = \sum_{i} E(\epsilon_{i}) - [(1-x)E(\epsilon_{\text{electrode}}) + xE(\epsilon_{SE})] \]

where \( x \) is the fraction of the solid electrolyte calculated from the normalized formula unit and \( \epsilon_{\text{electrode}} \) is the electrode composition. We normalized the formula units of each phase as if they contained one atom per formula unit. For example, the Na\(_{11}\)Sn\(_2\)Ps\(_{12}\) phase was regarded to have the formula unit Na\(_{1/2}\)Sn\(_{2/2}\)Ps\(_{1/2}\)S\(_{12/2}\). The introduction of the normalized formula units helps to determine the relative amount of the fraction of the phases. For the estimation of the electrical and ionic transport properties of byproducts from the decomposition reaction at the interface, we applied simple rules; the phase is regarded as electronically conductive if it possesses zero band gap and ionically insulative if a sodium ion is not included in the composition.

## RESULTS AND DISCUSSION

### Crystal Structure and Sodium Diffusion Path

**Figure 1.** Illustrations of (a) crystal structure of Na\(_{11}\)Sn\(_2\)Ps\(_{12}\), (b) Sn layer \((x, y, 4/8)\), and (c) P layer \((x, y, 3/8)\). Iso-surface (red) of sodium probability density distribution \( P = P_{\text{max}}/1024 \) at 800 K of (d) Sn layer \((x, y, 4/8)\) and (e) P layer \((x, y, 3/8)\). S ions are placed at the vertices of each polyhedron. Note that partial occupancies of sodium sites were not illustrated for the clarity of the crystal symmetry.

within a tetragonal space group I\(_4\)/acd:2 (no. 142, \( Z = 8 \)).\(^36,37,39\) The framework structure is constructed with isolated Sn\(_6\)S\(_4\) and Ps\(_4\) polyhedra. All the cation sites are arranged to form a three-dimensional grid with a distance of approximately 3.41 Å. The cation sublattice can be interpreted as an alternative layer-by-layer structure along the c-axis, consisting of Sn layers (including Sn\(_{6}\) \( \text{Figure 1b} \)) and P layers (including Ps\(_4\) \( \text{Figure 1c} \)). The Sn layers contain Sn (Wyckoff position 16e), Na\(_3\) (Wyckoff position 16d), Na\(_4\) (Wyckoff position 16c), and Na\(_5\) (Wyckoff position 16e) sites, while the P layers include P (Wyckoff position 8a), Na\(_1\) (Wyckoff position 16f), and Na\(_2\) (Wyckoff position 32g) sites. It should be noted that there are apparent vacant sites (Wyckoff position 8b) in the P layers, indicated by white spheres, which were reported to be important hopping sites for sodium diffusion by Duchardt et al.\(^57\) All the sodium sites are octahedrally coordinated by six sulfur ions, and each Na\(_n\) octahedron is connected through face-sharing, while the vacant sites are coordinated by eight sulfur ions forming a cubic-like structure (Figure 1a). Note that the excessive number of sodium sites (96 sites) compared with the available sodium ions (88 ions) causes the partial occupation of the sodium sites, indicating the presence of vacancies in sodium sites even in the pristine composition.

It should be noted that although the probability density of Na ions provides an intuitive picture of the diffusion path, this analysis is not sufficient to obtain quantitative understandings of the diffusion path. In particular, the low value of the probability density does not necessarily indicate the inactivity of the sites because intermediate sites for ion migration are less frequently occupied but actively participate in the diffusion. Therefore, in the following section, we provide more detailed interpretations of the diffusion behaviors in Na\(_{11}\)Sn\(_2\)Ps\(_{12}\) by analyzing the occupancies and rates of sodium ion hopping at each site.
Diffusion Mechanism in Na$_{11}$Sn$_2$PS$_{12}$. The ionic conductivity of sodium in Na$_{11}$Sn$_2$PS$_{12}$ at 300 K was estimated from a series of AIMD simulations. In Figure 2a, the diffusivities at elevated temperatures (every 100 K from 700 to 1300 K) are displayed as a function of temperature based on Arrhenius behavior with the extrapolated value at 300 K. Considering the tetragonal symmetry of Na$_{11}$Sn$_2$PS$_{12}$, each directional component along $a$-, $b$-, or $c$-direction in the overall diffusivities could be separately examined. And, the corresponding ionic conductivities at 300 K and activation energies are summarized in Table 1. It was found that both the overall and directional ionic conductivities were approximately 2.4 mS/cm at 300 K with an activation energy of 0.248 eV, demonstrating the fast and isotropic sodium diffusion in Na$_{11}$Sn$_2$PS$_{12}$, in good agreement with the previous study.36

To investigate the sodium diffusion mechanism in detail, the site occupancies and hopping rates obtained from the AIMD results were carefully analyzed for all the available sodium sites. The site occupancy is a measure of the probability that a sodium ion occupies the specific sites, thus, can be rationally converted to the site energy.18,63 In Figure 2b, the site occupancies by sodium are plotted as a function of temperature. As expected from the probability density analysis in Figures 1d–e and S2, all five sodium sites (Na1 to Na5) were observed to be primarily occupied with the occupancy ratio of higher than 70% for all the simulated temperatures. A slightly lower value of occupation for the Na2 and Na3 sites than others is due to the stronger repulsive force by P$^{5+}$ ions than by Sn$^{4+}$ ions, since those sites are placed at the first-neighboring grid points of PS$_4$ (Figure 1). These relatively low occupations of Na2 and Na3 sites were consistently observed in the previous studies as well.36,38,39 For the 8b vacant sites, we obtained a significantly low value of site occupancy by the sodium. In particular, the occupation of the vacant sites was almost zero at 700 and 800 K, even though these temperatures are much higher than the practical operating temperature of batteries. Moreover, our further DFT energy calculations with a sodium ion in the 8b vacant site resulted in the unstable state with more than 1 eV higher than the state without the 8b site occupation. It should be noted that occupation of the 8b site by sodium ions was not energetically stable, so we were forced to fix the single sodium ion to remain placed in the 8b site to estimate the instability, or the sodium ion is moved out to near sodium sites such as Na2 or Na3. Moreover, even if we initially put one sodium ion in the 8b site with fully occupied sodium around all six sodium sites, four Na$_2$ and two Na$_3$ sites, of the 8b cubic, the sodium ion moves out of the 8b sites by pushing one of the sodium ions in the face-sharing octahedron during the relaxation.

Nevertheless, it is noteworthy that the results on the occupancy of the 8b vacant site are different from previous works,38–40 where the site occupancies of 8b sites were found to be about 10–20% from single crystal X-ray diffraction data. It is uncertain at this moment what caused the apparent difference between the previous experimental works and our results here. Given the unequivocal picture from both AIMD simulations and the first-principles energy calculations along with the additional confirmation simulations (Figure S3), the ground-state structure of Na$_{11}$Sn$_2$PS$_{12}$ would not contain significant sodium occupation at 8b sites at room temperature. We suspect that the probed occupation of the vacant site by experiments could originate from potential metastable states of the material such as off-stoichiometry, locally formed unstable sodium arrangements, local mismatch of lattices, or native defects, which can cumulatively stabilize the 8b sites and were not considered in our crystal model (please see the further discussion in Supporting Information, Figures S4–S6). Indeed, the instability of 8b occupation by sodium ions, which was higher than 1 eV in our ground-sate structure model, was reduced to 0.5 eV from our rough calculations assuming various metastable states. However, the detailed study on these possible scenarios is beyond the scope of this study and should be investigated further in the future.

In conjunction with the analysis of site occupancies, the hopping rates at each crystallographic site can serve as an important measure in understanding the diffusion mechanism. We counted the number of sodium-ion hoppings occurring at the center of each site for the entire simulation times and normalized it by the time scale of 1 s. The results are plotted as a function of temperature in Figure 2c. The hopping rates of all the sodium sites are comparable, implying that they contribute almost equally to the diffusion. These results are consistent with the $^{23}$Na MAS NMR (magic angle spinning nuclear magnetic resonance) spectrum presented by Duchardt et al.;37 they observed no spinning sidebands, which indicates no immobile sodium ions in the structure. The hopping rates increase with temperature because of the higher thermal vibration rates at higher temperatures; however, no noticeable difference was found among different sodium sites. In contrast,

Table 1. Na Ionic Conductivities at 300 K and Activation Energies for Na Diffusion in Na$_{11}$Sn$_2$PS$_{12}$

<table>
<thead>
<tr>
<th>Direction</th>
<th>$\sigma_{Na}$ [mS/cm]</th>
<th>$E_a$ [eV]</th>
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<tbody>
<tr>
<td>overall</td>
<td>2.4</td>
<td>0.248 ± 0.013</td>
</tr>
<tr>
<td>ab-direction</td>
<td>2.4</td>
<td>0.248 ± 0.016</td>
</tr>
<tr>
<td>c-direction</td>
<td>2.3</td>
<td>0.248 ± 0.012</td>
</tr>
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Figure 2. Na diffusion behaviors of pristine Na$_{11}$Sn$_2$PS$_{12}$. (a) Arrhenius plots for Na$_{11}$Sn$_2$PS$_{12}$. The results at 300 K were extrapolated. (b) Occupancies and (c) hopping rates of Na and the vacant sites.
we did not observe any visible ionic hopping through the center of the 8b vacant site below 800 K, and high thermal energies (>900 K) were required to activate the hopping. With further confirmation of the results at 700 K (Figure S3), we think that the 8b vacant site is unlikely to participate in the overall sodium diffusion process in this structure at room temperature. The observed inactiveness of 8b sites is not consistent with the previous claim by Duchardt et al.37

We further attempted to estimate the stability of the 8b site by performing the activation barrier calculations for sodium ion migration by the nudged elastic band (NEB) method (Figure S7). While these NEB calculations provide the kinetic information regarding the sodium ion migrations, they can also offer information about the metastability of the intermediate sites within the path. Figure S7a illustrates the most representative migration path for sodium ions near the 8b sites with the calculated activation barriers. In the case of not passing through the 8b sites, the migration barriers for the sodium ion are as low as ~0.2 eV, indicating fast diffusion kinetics. However, as we intentionally move sodium ions along the path systematically closer to 8b sites, we could observe that the activation barrier significantly increases from ~0.6 eV (Figure S7b: slightly passing through the edge of the 8b site) to ~1.2 eV (Figure S7c: passing through the center of the 8b site). Substantially high activation barriers along the 8b sites (Figure S7b–c) compared with those between adjacent sodium sites (Figure S7a) indicate the kinetic inactiveness of the 8b sites for sodium diffusion as presented in Figure 2c. Even though relatively small activation energies via the surroundings (Figure S7b, ~0.6 eV) than that through the center (Figure S7c, ~1.2 eV) suggests a potential possibility of the 8b sites for the diffusion via passing through the surroundings, we observed nearly negligible contribution for both mechanisms in AIMD simulations at 700 K. Only two migrations of Figure S7b and zero migration of Figure S7c were observed, while S89 times of hoppings such as Figure S7a occurred in 80 ps of simulation time at 700 K. It is believed that the facile sodium diffusion in Na11Sn2PS12 is mainly attributable to the well-spread and partially occupied sodium sites forming three-dimensional diffusion paths with similar site energies and hopping rates. The isotropic diffusion channels throughout the material would benefit the practical diffusivity of this material, which would be less dependent on the orientations of each powder/grain in the pelletized powder or polycrystalline solid electrolyte.

Factors Affecting Sodium Diffusion Kinetics in Na11Sn2PS12-Type Conductors. To comprehend the factors affecting the sodium ionic conductivity of Na11Sn2PS12-type conductors, further simulations were performed for structures with variations in the sodium ion concentrations or the substitution of Sn sites. Figure 3a–b comparatively display the changes in the diffusivities in the Arrhenius plots as a result of the additional sodium ion vacancy/interstitial and the substitution of Sn sites. Figure S3a–b comparatively display the changes in the diffusivities in the Arrhenius plots as a result of the additional sodium ion vacancy/interstitial and the substitution of Sn sites by Si or Ge, respectively, which are also summarized in Table 2. Interestingly, it was found that the effect of additional vacancy or sodium interstitial in the structure is negligible on the sodium diffusion in Na11Sn2PS12-type conductors; the estimated ionic conductivities and activation energies were almost unchanged from those of the pristine structure. It is in contrast to previous reports on Na3PS4-type conductors demonstrating that the ionic con-

![Figure 3](image-url)
ductivities were drastically increased by introducing a small amount of sodium vacancy/interstitial.33,34 We suspect that this distinct behavior of Na_{11}Sn_{2}PS_{12} originates from the presence of inherent sodium disorder along with the partial occupancy in the crystal structure. Unlike the crystal structure of Na_{3}PS_{4}-type conductors, Na_{11}Sn_{2}PS_{12} contains large amounts of partially occupied sodium sites and thus does not require the formation of extra sodium vacancy/interstitial to exert superionic conducting properties.

On the other hand, Figure 3b illustrates that the substitution of the Sn site with Si or Ge severely impedes the sodium diffusion. The sodium ionic conductivity decreased by approximately one-fourth (0.6 mS/cm) and one-eighth (0.3 mS/cm) for the Ge and Si analogues, respectively. In order to elucidate this behavior, we first examined the structural alternation caused by the substitutions as tabulated in Table 3. It reveals that the substitutions of Sn sites with Ge or Si accompany noticeable reductions in the crystal volumes from 5192 to 5028 and 4962 Å³, respectively. The reduction of the crystal volume is primarily attributed to the reduced volume for the MS_{4} polyhedron (M = Sn (7.32 Å³), Ge (5.96 Å³), Si (5.21 Å³)); however, it also leads to the substantial reduction in the sodium channel volume from 5039 to 4896 and 4843 Å³, respectively. It implies that the reduction in the ionic conductivity with the substitutions of Si and Ge is likely due to the shrinkage of the sodium channel for diffusion. Additionally, we attempted to verify the chemical effect of the substitution excluding the size effect by carrying out AIMD simulations for the substituted structures but within the fixed lattice parameters of the pristine structure (Figure S8). The Sn-site substitutions within the fixed cell did not result in the reduction of the sodium diffusivity but rather slightly increased the diffusivity, implying that the retarded sodium diffusion does not originate from any chemical influence of the substitutes.

In order to further confirm the effect of reduced lattices on sodium diffusion behaviors, we systematically examined the influence of the lattice size on sodium diffusion within the Na_{11}Sn_{2}PS_{12} structure at extended scales (Figure 3c–d). The lattice constants (a, b, and c) were isotropically scaled from −4% to +4% based on those of the pristine Na_{11}Sn_{2}PS_{12} structure. Figure 3c represents the temperature-dependent diffusivities for the four representative cases (−4, −2, 0, +2, and +4%). Additionally, in Figure 3d, the extrapolated ionic conductivities at 300 K are plotted with respect to the changes in the lattice size. The ionic conductivities systematically increase with increasing size of the lattice, which agrees with the findings above. When plotted together with the results of Si and Ge substitutions with the corresponding lattice sizes and the conductivities, they lies in the general trend following the simple correlation between the conductivity and the size. From these results, we can conclude that the retarded sodium diffusion in the case of the Si and Ge substitution was mainly due to the reduction of the lattices. Nevertheless, it was observed that much less reduction in the ionic conductivity is caused by the shrinkage of the lattice from a certain point from 2% to 4% size reduction. From a close inspection of the sodium diffusion in this case, we found that sodium ionic hopping through the 8b vacant site becomes active when the major sodium channels are narrowed to this level as illustrated in Figure S10. The additional diffusion path offered by the 8b vacant site can mitigate the effect of the shrinkage in the major sodium ion channel, thus slightly aiding in the overall diffusion, playing the role of buffer region. This type of buffering effect might be beneficial for maintaining its superior transport properties even under extreme local compressive stresses.

### Phase Stability, Electrochemical Stability, and Interfacial Compatibility

For the practical use of Na_{11}Sn_{2}PS_{12} as a solid electrolyte, other important prerequisites include phase stability, electrochemical stability, and interfacial compatibility with electrode materials. To understand the general stability of the Na_{11}Sn_{2}PS_{12} phase, the quaternary Na_{x}Sn_{y}P_{z}S_{w} phase diagram was examined considering all the known stable phases in the given chemical space. Our calculation revealed that Na_{11}Sn_{2}PS_{12} is thermodynamically stable at 0 K against the potential decomposition reaction of Na_{11}Sn_{2}PS_{12} → Na_{4}SnS_{4} + Na_{4}PS_{4} with a positive reaction energy of approximately 3 meV/atom. The predicted decomposition reaction is consistent with that previously reported by Yu et al.33 In addition, we evaluated the phase stability of Na_{11}M_{2}PS_{12} (M = Si, Ge) against the decomposition reaction of Na_{11}M_{2}PS_{12} → Na_{4}MS_{4} + Na_{4}PS_{4}. Calculated values of both decomposition reactions were 6 meV/atom. The positive reaction energies indicate the new substituted phases are likely to be stable against the decomposition reactions. Even though the estimated stabilities are small and within the calculation error range, the configurational entropy from intrinsic sodium disordering in Na_{11}Sn_{2}PS_{12} guarantees the stability at elevated temperatures.35 It should be noted that most solid electrolyte materials, unlike Na_{11}Sn_{2}PS_{12}, were predicted to be unstable at 0 K and believed to be stabilized with the help of configurational or vibrational entropy at high temperature.57,68 The stability of Na_{11}Sn_{2}PS_{12} was further examined upon the applied voltage. In Figure 4a, the decomposition reaction energies of Na_{11}Sn_{2}PS_{12} are plotted as a function of voltage vs Na/Na^{+} as obtained from the sodium grand potential phase diagram in the quaternary Na_{x}Sn_{y}P_{z}S_{w} chemical space. It is observed that the Na_{11}Sn_{2}PS_{12} phase is stable within the range 1.16–1.92 V, however, electrochemically decomposes when the voltage is applied outside this window for both the reductive and oxidative environment. Given the sodium grand potential phase diagram, which describes the system open to a solid reservoir, the reductive reaction involves the formation of sodium binary phases such as Na_{4}SnS_{4}, Na_{3}P, and Na_{3}S below 0.10 V, while the oxidative decomposition produces Sn_{2}P_{2}S_{7}, and S above 3.40 V. The narrow electrochemical window of Na_{11}Sn_{2}PS_{12} implies that an appropriate selection of

### Table 3. Structural Parameters of Na_{11}M_{2}PS_{12} (M = Si, Ge, Sn)

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<tr>
<td>Na_{11}Si_{2}PS_{12}</td>
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<td>13.56</td>
<td>26.96</td>
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<td>90.1</td>
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<td>5132</td>
<td>7.32</td>
<td>4.52</td>
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</tr>
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*Obtained from radial distribution function of AIMD data (Figure S9). (Na channel volume) = (unit cell volume) − 16 × (MS_{4} volume) − 8 × (PS_{4} volume).
As an elemental step for selecting suitable electrode materials, we investigated the thermodynamic compatibility of the interfaces between Na$_{11}$Sn$_2$PS$_{12}$ and two representative electrode materials, Na metal for the anode (0 V vs Na/Na$^+$) and TiS$_2$ for the cathode (~1.7 V vs Na/Na$^+$). It is important to note that the decomposition reactions at the interfaces can occur in various ratios of Na$_{11}$Sn$_2$PS$_{12}$ to electrode materials because of the complicated nature of interfaces. Therefore, the decomposition reactions with various ratios should be considered to probe the interfacial compatibility. In Figure 4c, the reaction energy of mutual decomposition at the interfaces is plotted as a function of the fraction of Na$_{11}$Sn$_2$PS$_{12}$. Our calculation predicted the potential occurrence of decomposition reactions at both interfaces. However, the relatively small interfacial reaction energy between TiS$_2$ and Na$_{11}$Sn$_2$PS$_{12}$ (blue line) suggests that the interfacial reaction might be kinetically inhibited by the sluggish nature of the solid-state reactions.

The relatively good compatibility can be rationalized by the fact that the redox potential of the TiS$_2$ cathode is within the stable electrochemical window of Na$_{11}$Sn$_2$PS$_{12}$. In contrast, at the interface with Na metal, Na$_{11}$Sn$_2$PS$_{12}$ is expected to spontaneously degrade with a substantial reaction energy of ~0.38 eV/atom. The decomposition reactions yielded various phases at the interface between Na and Na$_{11}$Sn$_2$PS$_{12}$. Considering that the electronically insulated and ionically conductive phases are believed to build desirable interfaces by passivating the interface from the decomposition,$^{12,60-68}$ we estimated the fractions of by-products of electronically conductive and ionically insulative phases produced to examine the stability of the interface. In Figure 4d, the fractions of electronically conductive and ionically insulative phases produced from the decomposition reactions are displayed as a function of the fraction of Na$_{11}$Sn$_2$PS$_{12}$. Electronically conductive Na−Sn alloys such as Na$_{13}$Sn$_4$ and Na$_5$Sn$_4$ were observed to be formed at the interface; these alloys are detrimental to the interface stability because they hinder surface passivation. Moreover, Sn$_2$P$_3$ and P, which are expected to exhibit low sodium ionic conductivity, would block the ionic paths and increase the resistivity. These results are consistent with the X-ray photoelectron spectroscopy (XPS) results performed by Yu et al., who observed Na$_3$S and reduced Sn species at the interface between Na metal and Na$_{11}$Sn$_2$PS$_{12}$. For comparison, we examined Na$_3$PS$_4$ using the same approach, as shown in Figure S11. The interface between Na metal and Na$_3$PS$_4$ is more likely to be passivated from the decomposition reaction because of the major decomposition phases with electronically insulative nature without a Sn source in the electrolyte material. However, it should be noted that some decomposed phases with a small band gap could potentially possess non-negligible electronic conductivity. For example, the interface between Na$_3$PS$_4$ and Na metal was observed to be continuously degraded because Na$_3$P is produced at the interface; this phase has a small band gap of 0.405 eV$^{64}$ and 0.76 eV$^{22}$ from the calculations based on PBE and hybrid functionals, respectively. We believe that this could be a potential reason why the previous successful experimental reports employed not only Na$_3$PS$_4$ as a buffer layer but also Na−Sn alloy as an anode material, which could avoid substantial side reactions at the interface.\(^{39}\)

**CONCLUSION**

Comprehensive investigations on the recently discovered Na$_{11}$Sn$_2$PS$_{12}$ superionic conductor were performed using first-principles calculations. Our AIMD simulations indicate that the sodium diffusion in Na$_{11}$Sn$_2$PS$_{12}$ is nearly isotropic with a high ionic conductivity of 2.4 mS/cm at 300 K. Analyses of the site occupancies and hopping rates demonstrated that all the sodium sites actively participate in the diffusion with well-distributed sodium vacancies. In contrast, the vacant sites (8b sites) that were argued to be important for the fast sodium conduction were shown to be inactive in the diffusion without the occupation of sodium in the site. In addition, the effect of
the incorporation of additional sodium vacancy/interstitial was negligible on the ionic conductivity; in contrast, the isovalent substitution of Sn by Si or Ge severely retarded the sodium diffusion. It primarily stems from the reduced lattices, suggesting that improvement of the ionic conductivity could be achieved in expanded lattices. From thermodynamic calculations using phase diagrams, the Na$_{1.7}$Sn$_{0.3}$PS$_{4.12}$ phase was estimated to be stable even at 0 K, unlike other sulphide-based electrolyte materials. A narrow electrochemical window of 1.16–1.92 V was determined using a Na grand potential phase diagram, indicating that careful selection of electrode materials is required with consideration of the decomposition reactions at the interfaces. The presence of Sn in Na$_{1.7}$Sn$_{0.3}$PS$_{4.12}$ was revealed to produce electronically conducive phases at the interface with Na metal, leading to progressive deterioration of the interface. We believe that our comprehensive first-principles investigations provide a fundamental understanding of this new class of solid electrolytes as well as potential strategies for the further development of high-performance solid-state sodium electrolytes.

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