# Data-Driven Theoretical Design of Anion Cluster-Based Sodium Antiperovskite Superionic Conductors

Chaohong Guan, Huirong Jing, Yu Yang, Runxin Ouyang, and Hong Zhu\*

Cite This: ACS Appl. Mater. Interfaces 2024, 16, 70665–70674



ACCESS	III Metrics & More	E Article Recommendations	s) Supporting Information

**ABSTRACT:** Sodium antiperovskite materials (APs) are a promising class of solid-state electrolytes owing to their high structural tolerance and good formability. However, few APs have been synthesized experimentally, indicating the necessity of exploring potential chemical spaces with higher ionic conductivities. Herein, through a combined particle swarm optimization algorithm, high-throughput first-principles calculations, ab initio molecular dynamics, and long time-scale machine-learning molecular dynamics simulations, strategies based on site-exchanging and anion clusters are shown to simultaneously enhance the thermal stability and sodium diffusivity in the designed APs. Among these APs, the highest theoretical ionic conductivity of 39.05 mS/cm is achieved with Na<sub>3</sub>BrSO<sub>4</sub> at room temperature due to the strong coupling of cluster rotation and sodium migration. We highlight that not only the rotation dynamics but also its coupling with Na



diffusion contribute to the high ionic conductivity, as confirmed by the proposed local difference frequency center to evaluate the coupling degree. Our work designs promising site-exchanging APs and offers insights into the coupling between anion rotation and cation migration, which can effectively guide the design of superionic conductors with cluster rotation dynamics.

KEYWORDS: sodium antiperovskite superionic conductors, site exchanging, anion clusters, rotation dynamics, coupling degree

# 1. INTRODUCTION

The development of sodium-ion batteries has been desired because of the superior characteristics of sodium compared to lithium, including their lower cost and higher earth abundance.<sup>1,2</sup> Sodium metal batteries are also facing safety issues caused by the growth of Na dendrites and the reactions between the sodium anode and organic liquid electrolytes.<sup>3</sup> Thus, all-solid-state sodium batteries (ASSSBs) are receiving keen interest in offering better safety and potentially higher energy density by matching Na metal and high-voltage cathodes. As a critical part of ASSSBs, a significant amount of studies<sup>4-7</sup> have been conducted to explore promising solid sodium electrolytes. The sodium ionic conductivities were improved from  $10^{-6}$  to  $10^{-3}$  S/cm<sup>8</sup> by understanding the structure-cation mobility relationships and leveraging important features for sodium superionic conductors, such as the concerted ion migration,<sup>9</sup> the body-centered cubic-like anion framework<sup>10</sup> and the concentration of vacancy defects.<sup>1</sup> Though some electrolytes show relatively high ionic conductivities (such as  $Na_{2.88}Sb_{0.88}W_{0.12}S_4$ ,  $\sigma_{RT} = 32$  mS/ cm),<sup>12</sup> most sodium oxides (e.g., NASICON-Na<sub>3</sub>Zr<sub>2</sub>Si<sub>2</sub>PO<sub>12</sub> with  $\sigma_{\rm RT} = 0.67 \text{ mS/cm})^{13}$  and sulfides (e.g., Na<sub>10</sub>SnP<sub>2</sub>S<sub>12</sub> with  $\sigma_{\rm RT}$  of 0.4 mS/cm)<sup>14-16</sup> show lower ionic conductivities at room temperature (RT) than the Li-ion counterparts (such as  $\sigma_{\rm RT} = 7 \text{ mS/cm}$  of Li<sub>10</sub>SnP<sub>2</sub>S<sub>12</sub>).<sup>17</sup> Thus, developing novel sodium solid-state electrolytes (SSEs) with higher RT ionic

conductivities is desirable and worth pursuing from both experimental and theoretical perspectives to further optimize the performance of ASSSBs (the possible increased active materials loading and the reduced overall impedance).<sup>18</sup>

Recently, an interesting phenomenon, which assists ion migration by possible rotational dynamics of anion polyanions, has received renewed consideration.<sup>19–22</sup> Some sodium solid-state electrolytes with polyanions show distinct rotational freedom for polyanions, which explains why the  $\sigma_{\rm RT}$  of Na<sub>11</sub>Sn<sub>2</sub>PS<sub>12</sub> and Na<sub>11</sub>Sn<sub>2</sub>PSe<sub>12</sub> (1.4–3.7 and 3.0 mS/cm, respectively) is almost an order of magnitude higher than that of Na<sub>11</sub>Sn<sub>2</sub>SbS<sub>12</sub> (0.5–0.6 mS/cm). Moreover, the facile rotation of PS<sub>4</sub><sup>3–</sup> and PSe<sub>4</sub><sup>3–</sup> anions is directly coupled to sodium mobility, while there is no obvious SbS<sub>4</sub><sup>3–</sup> rotation at the experimental temperatures in the less conductive phase (Na<sub>11</sub>Sn<sub>2</sub>SbS<sub>12</sub>). Therefore, more studies have emerged on the rotational dynamics of polyanions or anion clusters in sodium SSEs (Na<sub>3</sub>PS<sub>4</sub>, Na<sub>2</sub>BH<sub>4</sub>NH<sub>2</sub>, Na<sub>3.5</sub>Si<sub>0.5</sub>P<sub>0.5</sub>Se<sub>4</sub>, and NaCB<sub>11</sub>H<sub>12</sub>).<sup>23,24</sup> In addition, incorporating anion clusters

Received:October 1, 2024Revised:November 20, 2024Accepted:November 26, 2024Published:December 12, 2024







Figure 1. Flowchart of the high-throughput design procedure for identifying sodium antiperovskite SSEs.

into an argyrodite framework<sup>22</sup> (Li<sub>6</sub>POS<sub>4</sub>(SH) and Li<sub>6.25</sub>PS<sub>5.25</sub>(BH<sub>4</sub>)<sub>0.75</sub>) results in increased theoretical ionic conductivities of 82 mS/cm and 177 mS/cm at room temperature, respectively, approaching the criteria of the so-called advanced superionic conductors (ASIC, whose ionic conductivity is larger than 100 mS/cm).<sup>25</sup>

Herein, motivated by the urgent need for sodium electrolyte development with higher ionic conductivity and the great potential of anion dynamics on cation mobility, we designed novel antiperovskites (APs) with rotational anion clusters using the particle swarm optimization (PSO) algorithm and high-throughput first-principles calculations. The thermodynamic and dynamic properties of these cluster-based APs were systematically investigated, and their synthesizability was also examined using the Gibbs free energy. Moreover, the trajectories and rotational dynamics from typical and restricted molecular dynamics simulations were analyzed to gain insight into the correlation between anion rotation and cation migration. It is expected that our designed APs with anion clusters will open up potential chemical spaces with antiperovskite structures and effectively guide the improvement of other superionic conductors.

## 2. COMPUTATIONAL METHODOLOGY

A multistep high-throughput design procedure was adopted, as shown in Figure 1. By introducing different anion clusters into the antiperovskite structural framework, the tolerance factor was initially adopted to evaluate the stability. The particle swarm optimization (PSO) algorithm combined with density functional theory (DFT) calculations was applied to search the ground-state structure of cluster-based APs. Then, ab initio molecular dynamics (AIMD) simulations were conducted to calculate the ionic conductivities (the reliability of the DFT and AIMD methods was verified by the lattice parameters and activation energies provided in the Supporting Information, Figure S1), and machine-learning MD was further performed to confirm the room-temperature ionic conductivity. Besides, for the selection of anions, we first collected various divalent (B) and monovalent (A) anion clusters from the literature. In total, there were 120 Na<sub>3</sub>BA and 120 Na<sub>3</sub>AB based on different combinations of A and B anions. Then, the tolerance factors (t), energy above the hull, and phonon dispersion were calculated to screen the anion clusters that can be stable in the antiperovskite lattice framework. Finally, AIMD simulations were conducted to confirm the anion clusters, which can promote sodium migration and improve ionic conductivity.

2.1. Searching the Structure of Cluster-Based Antiperovskites. To confirm the reorientation of the anion clusters, the ground-state structures were determined using the particle swarm optimization (PSO) algorithm implemented in the CALYPSO package,<sup>26</sup> which was adopted to predict the structures of cluster-based antiperovskites. Notably, the anion clusters are treated as an absolute "element" at the beginning of the structural search, and the structures of the studied anion clusters are shown in Figure S2. During the structural search, 20-30 initial structures are constructed in a population based on the different space groups, which will be optimized until the energy  $(10^{-5} \text{ eV})$  and force (0.03 Å/eV) convergence criteria are reached. The 60% optimized structures with the lowest energies were selected to generate updated structures with different symmetries in the next generation. When the structures with the lowest energies did not change after 10-30 generations of optimization, they were selected for the following calculations.

**2.2. Calculating the Properties of the Cluster-Based Antiperovskites.** Further high-accuracy structural optimizations for the properties of these cluster-based antiperovskites were conducted using the VASP code based on the PAW method.<sup>27</sup> The exchange-correlation potential for the overall lattice optimization is described by the Perdew–Burke–



Figure 2. Tolerance factor of sodium antiperovskites, including (a) Na<sub>3</sub>BA and (b) Na<sub>3</sub>AB. A and B represent monovalent and divalent anions, respectively.

Ernzerhof (PBE) generalized gradient approximant (GGA)<sup>28</sup> and the dispersion correction is considered by Grimme's semiempirical schemes. The energy cutoff is 520 eV for the plane wave expansion with a  $7 \times 7 \times 7$  Monkhorst–Pack *k*point mesh, and the energy and force convergences are set to  $10^{-6}$  eV and 0.01 eV/Å, respectively. The dynamic stability was characterized by phonon dispersion, which was calculated by the density functional perturbation theory (DFPT)<sup>29</sup> employed in the Phonopy code.<sup>30</sup> The hybrid functional (HSE06)<sup>31</sup> was adopted for the band gap calculations. Additionally, the details of ab initio molecular dynamics (AIMD) are provided in the Supporting Information.

2.3. Procedure for Fitting the Moment Tensor Potential (MTP). The machine-learning interatomic potential, moment tensor potential (MTP),<sup>31</sup> was trained based on the AIMD results with the NVT ensemble at different temperatures (300, 500, 700, 900, and 1100 K) and three strains (0, +0.05, and -0.05), similar to the work of Ong et al.<sup>32</sup> The details for the MTP are provided in Supporting Information. First, the system was heated from 0 K to the target temperature and equilibrated for 40 ps with a time step of 2 fs. Then, snapshots of different temperatures or strains were extracted from the last 20 ps at 0.1 ps intervals. Therefore, 3000 training structures  $(200 \times 15)$  were generated. Finally, we performed static calculations on these structures to obtain accurate energies and forces to prepare for MTP training. Notably, a kpoint density of at least  $100/Å^3$  was adopted for the static calculations. During the MTP training, we assigned weights of 100:1 for the energy and force data according to the work of Ong.<sup>32</sup> All training and MD simulations in this work are based on the Python Materials Genomics (pymatgen) library,<sup>33</sup> MLIP,<sup>34</sup> and LAMMPS.<sup>35</sup>

## 3. RESULTS AND DISCUSSION

**3.1. Structure and Stability of the Cluster-Based Sodium Antiperovskites.** Typical sodium antiperovskite structures (APs) have the formula Na<sub>3</sub>BA, where B and A usually represent divalent chalcogen anions and monovalent halogen anions (namely, B (-2) and A (-1) in Figure 1, such as Na<sub>3</sub>OCl), respectively. The framework is formed with corner-sharing octahedra, where the sodium ions occupy the corner sites of the octahedra, the divalent chalcogen anions

occupy the central sites of the octahedra, and the monovalent halogen anions occupy the vacant space between octahedra. To introduce anion rotation dynamics that potentially increase the ionic conductivity, in this work, common divalent anion clusters (SO<sub>4</sub><sup>2-</sup> and SeO<sub>4</sub><sup>2-</sup>) and monovalent anion clusters (OH<sup>-</sup>, ClO<sup>-</sup>, CN<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NH<sub>2</sub><sup>-</sup>, BH<sub>4</sub><sup>-</sup>, AlF<sub>4</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, BCl<sub>4</sub><sup>-</sup>, and  $AlH_4^{-}$ ) were considered for ions B (-2) and A (-1). The corresponding Goldschmidt factors (t) of these Na<sub>3</sub>BA (Figure 2a) indicate that there are 33 structures with suitable t values in the range of  $0.8-1.1^{36}$  (detailed values are listed in Table S1), which is an empirical criterion for the crystallographic stability of antiperovskite structures. For example,  $Na_3OBH_4$ , <sup>3737</sup>  $Na_3OAlH_4$ , and  $Na_3OBF_4$  with t values of 0.89, 1.09, and 1.05, respectively, have been experimentally or theoretically confirmed to be stable. Most importantly, exchanging the positions of anions A and B (Na<sub>2</sub>AB in Figure 1) leads to 31 additional cluster-based APs with a suitable t(Figure 2b), while a few studies have focused on the siteexchanged APs. Thus, with the assistance of PSO and highthroughput DFT calculations, the ground-state structures of cluster-based Na<sub>3</sub>BA and Na<sub>3</sub>AB are determined to further explore their potential as solid-state electrolytes.

The thermodynamic stabilities of these cluster-based APs are first evaluated by the energy above the hull  $(E_{hull})$ , which is defined by the decomposition energy of a structure into the most stable compounds, and a structure with a lower  $E_{hull}$ exhibits higher thermodynamic stability. In this work,  $E_{\rm hull}$  < 0.084 eV/atom is used as the criterion of thermodynamic stability, considering the successful synthesis of Na<sub>3</sub>OBH<sub>4</sub>  $(E_{\text{hull}} = 0.084 \text{ eV/atom})$  in the experiment.<sup>37</sup> Based on this criterion, we identified 32 thermodynamically stable and metastable APs (Figure S3). Among them,  $Na_3SeO_4X$  (X = F, Cl, and Br),  $Na_3AlH_4Y$  (Y = S, Se, and Te), and  $Na_3BF_4Y$  (Y = Se, Te) were converted to Na<sub>3</sub>XSeO<sub>4</sub>, Na<sub>3</sub>YAlH<sub>4</sub>, and Na<sub>3</sub>YBF<sub>4</sub> (labeled by blue lines in Figure S3) after optimization, respectively. In addition,  $Na_3BH_4Y$  (Y = S, Se, or Te) transforms into non-AP structures upon structural relaxation (see Figure S4a). Then, the dynamic stabilities of the remaining 21 thermodynamically stable APs were assessed. The phonon spectra (Figure S5) indicate that the 10 thermodynamically stable APs are also dynamically stable with no imaginary modes (such as  $Na_3XYO_4$ , X = Cl, Br; and Y



Figure 3. (a) Mapping of the dynamic stability of thermodynamically stable Na<sub>3</sub>BA and Na<sub>3</sub>AB. A gray, blue, or red square indicates that the structure is thermodynamically unstable ( $E_{hull} > 0.084 \text{ eV/atom}$ ) (gray box), thermodynamically stable ( $E_{hull} < 0.084 \text{ eV/atom}$ ) but dynamically unstable (blue box), or both stable thermodynamically and dynamically (red box), respectively. (b) Calculated band gaps of stable Na<sub>3</sub>BA and Na<sub>3</sub>AB based on the HSE06 hybrid functional, compared with NASICON and sulfides. (c) Calculated electrochemical stability windows of Na<sub>3</sub>BrSO<sub>4</sub>, Na<sub>3</sub>ClSO<sub>4</sub>, and Na<sub>3</sub>BrSO<sub>4</sub>.



Figure 4. (a) Arrhenius relationships for the designed superionic conductors, along with other reported sodium SSEs. The right plane shows the MSD of the anion clusters in Na<sub>3</sub>BrSO<sub>4</sub>, Na<sub>3</sub>ClSO<sub>4</sub>, and Na<sub>3</sub>BrSeO<sub>4</sub>. (b) Probability atomic density distributions. (c) Fitted Arrhenius relationship of Na<sub>3</sub>ClSO<sub>4</sub> based on MTP. (d) The driving force ( $\Delta G$ ) to form the designed candidates.

= S, Se). Overall, three Na<sub>3</sub>BA and seven Na<sub>3</sub>AB are screened with both thermodynamic and dynamical stabilities (Figure 3a), and their structures and lattice parameters are shown in Figure S4b and Table S2. In particular, the lattice constant of Na<sub>3</sub>OBH<sub>4</sub> is 4.56 Å, which is consistent with the theoretical value (4.57 Å)<sup>39</sup> and slightly smaller than the experimental value (4.63 Å).<sup>37</sup>

Besides, the HSE06 hybrid functional was used to calculate the band structures of stable  $Na_3BA$  and  $Na_3AB$  (Figure S6). The band gaps obtained are in the range of 3.0–6.6 eV (Figure 3b), which are comparable with the gaps of most NASICON

electrolytes and larger than the gaps of sulfides<sup>40–42</sup> (see Table S3 for detailed values). A sodium grand potential phase diagram was also constructed to further confirm electrochemical stability. For example, Na<sub>3</sub>BrSO<sub>4</sub> is oxidized to Br<sub>2</sub> and a Na<sub>2</sub>SO<sub>4</sub> phase with sodium extraction when the voltage is higher than 3.24 V (Figure S7a). The sodiation voltage of Na<sub>3</sub>BrSO<sub>4</sub> is 0.87 V, which decomposes into Na<sub>6</sub>S<sub>2</sub>O<sub>9</sub>, Na<sub>2</sub>S, and NaBr phases. Thus, the electrochemical window of Na<sub>3</sub>BrSO<sub>4</sub> is from 0.87 to 3.24 V, with a stable window of 2.48 V. Figure 3c shows that this window is larger than that of sulfides,<sup>43</sup> such as Na<sub>3</sub>PS<sub>4</sub> (1.06 V), Na<sub>10</sub>SnP<sub>2</sub>S<sub>12</sub> (0.86 V), or

 $Na_3PSe_4$  (0.3 V). Besides, other stable APs also have windows in the range of 1–2.87 V (Figure S7b), indicating that clusterbased electrolytes have better electrochemical stabilities and compatibilities with electrodes than the typical sodium sulfides.

3.2. Conductivity and Synthesizability of Cluster-Based Sodium Antiperovskites. AIMD simulations were conducted to explore the ionic conductivities of these stable candidates for electrolytes in solid-state batteries. According to the MSD of structures (Figure S8), only three site-exchanged structures (Na<sub>3</sub>BrSO<sub>4</sub>, Na<sub>3</sub>ClSO<sub>4</sub>, and Na<sub>3</sub>BrSeO<sub>4</sub>) exhibit the stable anion frameworks at simulated temperatures and the potential RT superionic conductivities, whose activation energies (0.15, 0.162, and 0.22 eV, respectively, as shown in Figure 4a) are lower or comparable to those of sodium sulfides (such as 0.22 and 0.24 eV for  $Na_7P_3S_{11}^{44}$  and  $Na_{11}Sn_2PS_{12}$ , respectively)<sup>45</sup> or NASICON electrolytes (such as 0.75 eV for  $NaZr_2(PO_4)_3$ ).<sup>46</sup> However, for others, such as  $Na_3ClSeO_4$  or Na<sub>3</sub>SAlH<sub>4</sub>, the almost horizontal MSD curves at 700 K suggest that the sodium atoms oscillate around the lattice site with extremely low ionic conductivities. Besides, Na<sub>3</sub>BrSO<sub>4</sub> exhibits the highest RT ionic conductivity of 39.05 mS/cm, which is orders of magnitude higher than that of typical antiperovskites  $(Na_3OX, X = Cl, Br, and I)$ <sup>37</sup> and the RT ionic conductivities of Na<sub>3</sub>ClSO<sub>4</sub> and Na<sub>3</sub>BrSeO<sub>4</sub> are 9.38 and 2.3 mS/cm, respectively. Given the similar antiperovskite structure to Na<sub>3</sub>OX, the increased ionic conductivities may be attributed to the special structure of cluster-based APs. The MSD curves for anion clusters (such as  $SO_4^{2-}$ , the right plane in Figure 3a) demonstrate that the edged O atoms have certain displacements, but no long-range migration occurs during AIMD simulations. This phenomenon is also visualized by the probability density distributions of O atoms (Figure 4b), which suggests that the oxygen atoms only rotate around the center atoms of clusters (S and Se atoms), exhibiting obvious anion rotational dynamics similar to those of Na<sub>11</sub>Sn<sub>2</sub>PS<sub>12</sub>,  $Na_{2.25}Y_{0.25}Zr_{0.75}Cl_6^{55}$  or  $Li_{3.25}Si_{0.25}P_{0.75}S_4^{2020}$  Notably, the limited probability density distribution of O atoms in Na<sub>3</sub>FSeO<sub>4</sub> with low ionic conductivity (Figure S9) indicates the reduced freedom for the rotation of anion clusters. Thus, anion rotation greatly contributes to sodium migration.

To the best of our knowledge, anion rotation may disappear at lower temperatures, leading to non-Arrhenius behavior for ion diffusion in the material.<sup>5</sup> Therefore, we fitted the ML-MTP (computational methodology) to reveal the possibility of anion rotation at RT and confirm whether non-Arrhenius behavior exists in our designed material. Figure S10 shows the mean absolute errors (MAEs) in energies (1.46 meV/atom) and forces (0.05 eV/Å) for the fitted MTP of Na<sub>3</sub>ClSO<sub>4</sub>. The smaller MAEs compared to previous studies<sup>47,48</sup> indicate a high accuracy for reproducing the DFT results of our fitted potential. To further confirm the accuracy of the MTP model, the lattice parameters are calculated as shown in Table S4, and the MTP is able to reproduce the DFT lattice parameters within an error of 0.8%. Besides, the radial distribution function (RDF) of Na<sub>3</sub>ClSO<sub>4</sub> was calculated using AIMD and MTP-based molecular dynamics simulations (Figure S11), and the results showed excellent agreement between the MTP and AIMD trajectories. Therefore, the fitted MTP model is suitable to describe the complex ion interactions in Na<sub>3</sub>ClSO<sub>4</sub>. Adopting this MTP in long-time MD simulations (100 ns) at different temperatures (300, 350, 400, 450, and 500 K), the fitted activation energy (0.163 eV, Figure 4c) is close to the AIMD results (0.162 eV, Figure 4a). In addition, long-time

MD simulations predicted that the diffusion coefficient of Na atoms at RT is  $7.07 \times 10^{-8}$  cm<sup>2</sup>/s (Figure S12a), which matched well with the AIMD extrapolated RT diffusion coefficient of  $6.98 \times 10^{-8}$  cm<sup>2</sup>/s. We also observed anion rotation at RT according to the 2D angular probability density distribution (Figure S12b). These observations indicate that non-Arrhenius behavior does not occur in Na<sub>3</sub>BrSO<sub>4</sub>.

We next studied the synthesizability of the designed SSE candidates by computing the driving force ( $\Delta G$ ) associated with each reaction, which follows a similar procedure to that outlined in previous work,<sup>49</sup> and  $\Delta G$  is the Gibbs free energy difference between the products and reactants at one temperature. The finite temperature effect was accounted for by using a machine-learning model based on the SISSO (sure independence screening and sparsifying operator) approach.<sup>50</sup> The negative  $\Delta G$  values for Na<sub>3</sub>BrSO<sub>4</sub> (-95 meV/atom at 500 K), Na<sub>3</sub>ClSO<sub>4</sub> (-51 meV/atom at 500 K), and Na<sub>3</sub>BrSeO<sub>4</sub> (-117 meV/atom at 500 K), shown in Figure 4d, suggest the large driving forces form these sodium electrolytes by the corresponding precursors, and Na3BrSeO4 shows the largest reaction driving force. Hence, we suggest that these SSEs can be promising for experimental syntheses. To further evaluate the synthesizability, the reaction energy  $(\Delta E_t)$  is defined as the energy change upon the reaction to form a phase of interest from its phase equilibrium compounds (details are provided in Supporting Information). The  $\Delta E_f$  values for Na<sub>3</sub>BrSO<sub>4</sub>, Na<sub>3</sub>ClSO<sub>4</sub>, and Na<sub>3</sub>BrSeO<sub>4</sub> are -0.81, -0.46, and -0.58 eV, indicating that these compounds can be likely synthesized by the spontaneous reactions of their phase equilibrium compounds. Besides, when  $E_{\text{hull}} = 0 \text{ eV}/\text{atom}$  (Na<sub>3</sub>ClSO<sub>4</sub>, as revealed by the phase diagram in Figure S13), the system lies on the convex hull, which is thermodynamically stable and can be possibly experimentally synthesized. The  $E_{\text{hull}}$  values of Na<sub>3</sub>BrSO<sub>4</sub> and Na<sub>3</sub>BrSeO<sub>4</sub> are larger than 0 with values of 0.072 and 0.05 eV/atom, respectively; thus, both systems are metastable based on the threshold for metastability ( $E_{\text{hull}} < 0.1$ eV/atom).

Further, the phonon dispersions indicate that both metastable compounds are dynamically stable and may be thermodynamically stable by the entropic contributions at elevated temperatures. Therefore, the temperature-dependent formation free energies were calculated to further confirm the synthesizability of metastable compounds with  $E_{\text{hull}} > 0 \text{ eV}/$ atom. The formation free energy  $(\Delta G_f)$  is defined as the difference between the free energies of the target compounds and their phase equilibrium compounds based on the calculations of lattice vibrational entropies. The temperaturedependent  $\Delta G_f$  of Na<sub>3</sub>BrSO<sub>4</sub> and Na<sub>3</sub>BrSeO<sub>4</sub> are shown in Figure S14, which indicates that both the compounds are entropically stabilized at elevated temperatures and that both materials are likely to be experimentally synthesized due to their negative formation free energies. For example, when the temperature is above 360 K, the  $\Delta G_f$  of Na<sub>3</sub>BrSO<sub>4</sub> is less than 0, indicating that Na<sub>3</sub>BrSO<sub>4</sub> can be synthesized by thermodynamic driving forces.

**3.3.** Conduction Mechanism of the Cluster-Based Sodium Antiperovskites. To further confirm the key factors contributing to the high ionic conductivities of the three superionic conductors, sodium migration events were analyzed using the function  $h_i$ , which identifies long-lived Na-ion displacements of at least a distance *a* occurring at a time window of  $t_w$  ( $t_w = t_a - t_p$ ):<sup>S1</sup>



**Figure 5.** Identified long-lived Na diffusion events in the supercell of  $Na_3BrSO_4$  at 700 K. For example, for the diffusion event of the fifth Na atom, the long-lived diffusion will begin at about 12 ps with a threshold distance (a) of 3 Å and a time window ( $t_w$ ) of 3 ps. Additionally, the diffusion events with a larger displacement (4 Å) are marked in red. (b) and (c) van Hove correlation functions at 700 and 900 K for Na atoms in  $Na_3BrSO_4$  during the AIMD process.



**Figure 6.** (a) Displacements of Na ions (black line) and neighboring anion clusters (SO<sub>4</sub>, blue lines) in Na<sub>3</sub>BrSO<sub>4</sub> at 700 K for the events labeled in red in Figure 4a. The corresponding trajectories are shown in (b), where the rotational direction of the anion clusters is highlighted by black arrows. Notably, the silver white and green balls represent the trajectories of Na ions and anion clusters, respectively. (c, d) Power spectra of Na (red) and anion clusters (blue) in Na<sub>3</sub>BrSO<sub>4</sub> and Na<sub>3</sub>FSeO<sub>4</sub>, respectively.

$$h_{i}(t; t_{p}, a, t_{a}) = \prod_{t'=(t_{a}-t_{p})/2}^{t_{a}/2} \theta(|r_{i}(t+t') - r_{i}(t-t')| - a)$$
(1)

where  $t_p$  and  $t_a$  represent the time windows of residence time and total time, respectively. The parameter *a* is the long-lived displacement during the total time window; more details are provided in Supporting Information. Figure 5 shows these long-lived Na diffusion events by plotting  $h_i$  vs time during the AIMD process at 700 K for every Na atom in the Na<sub>3</sub>BrSO<sub>4</sub> supercell, which includes 17 distinctive events with obvious time intervals when the threshold distance is 3.0 Å (red events represent the diffusion with a larger threshold distance of 4 Å). More diffusion events are found with the reduced threshold



**Figure 7.** (a) Reorientation autocorrelation function C(t) of the anion clusters in Na<sub>3</sub>BrSO<sub>4</sub>, Na<sub>3</sub>BrSO<sub>4</sub>, and Na<sub>3</sub>FSeO<sub>4</sub> at 700 K. (b) Helmholtz free energy surfaces of SO<sub>4</sub><sup>2-</sup> in Na<sub>3</sub>BrSO<sub>4</sub>, and others in Figure S20. The Helmholtz free energy surface A as a function of angles  $\theta$  and  $\varphi$  (Figure S12) was computed according to  $A(\theta, \varphi) = -k_B T \ln[\rho(\theta, \varphi)]$ , where  $k_B$  is the Boltzmann constant, T is the temperature, and  $\rho(\theta, \varphi)$  is the probability density distribution of anionic ligands of anion clusters from AIMD simulations. (c) Reorientation autocorrelation function C(t) of the anion clusters in Na<sub>3</sub>BrSO<sub>4</sub> and Na<sub>3</sub>NH<sub>2</sub>Te. (d) Activation energies and local difference frequency center (LDFC) for different systems.

distance (2.5 Å); the number of diffusion events is also significantly larger than the other two conductors (Na<sub>3</sub>ClSO<sub>4</sub> and Na<sub>3</sub>BrSeO<sub>4</sub>, Figure S15). Therefore, the identified number of long-lived events explains the relatively high ionic conductivity of Na<sub>3</sub>BrSO<sub>4</sub>. Besides, we summed the number of sodium atoms with the identified diffusion events occurring simultaneously to analyze the interaction between different Na atoms. As displayed in Figure S16a, during the same time window, simultaneous diffusion events mainly involve one, two, and three sodium atoms. We visualized some dual-atom or triatomic diffusion events, as shown in Figure S16b, where the adjacent sodium atoms undergo migration, and the migration of one atom among them impinges upon the previous position of the other atoms. This behavior of sodium indicates that the sodium diffusion events are correlated in space, and the van Hove correlation function (Figures 5b and S16c) confirms the concerted migration in the three conductors at 700 K. However, the concerted migration will be weak with increasing temperatures (900 K, Figure 5c), which is attributed to the strengthened rotational dynamics of the anion clusters at elevated temperatures. Additionally, the comparable extent of the concerted migrations of Na<sub>3</sub>BrSO<sub>4</sub> and  $Na_3BrSeO_4$  (Figure S16c) cannot explain the conductivity difference between the two structures at 700 K. Combining the

above analysis, we conclude that the concerted migration is not the main reason for the high ionic conductivities.

To demonstrate the effects of the rotational dynamics of anion clusters on Na diffusivity, the displacements of sodium diffusion events (Na5, Na14, and Na16) in Na3BrSO4 were studied, as labeled in red in Figure 5a (the displacements of the neighboring anion rotation are also calculated), which indicates that the migration of sodium atom is synchronized with the rotation of neighboring anion clusters, and the large displacements (about 3 Å) of edged atoms (O in  $SO_4^{2-}$ ) show the large rotational angles of these anion clusters. This synchronization between the Na migration and anion rotation can also be observed in Na<sub>3</sub>ClSO<sub>4</sub> and Na<sub>3</sub>BrSeO<sub>4</sub> (Figure S17a). To provide a more detailed view of this cation-anion coupling mechanism, Figure 6b highlights the diffusive trajectories of Na ions (silvery, Na5, Na14, and Na16) and the neighboring anion clusters (green) during the same time windows; the same displacement directions of Na migrations and anion rotations imply the fast Na diffusion promoted by the anion rotation. As identified by the vibrational spectra calculated by the Fourier transform of the velocity autocorrelation function (Figures 6c and S17c), the peaks in the low-frequency region represent the sodium vibrational and anion rotational modes (Figure S18), which exhibit great potential for transferring the momentum of anion rotations to

the sodium migration (a phenomenon observed in previous studies of Na<sub>4</sub>SiSe<sub>4</sub><sup>23</sup> and Li<sub>3.25</sub>[Si<sub>0.25</sub>P<sub>0.75</sub>]S<sub>4</sub>).<sup>20</sup> Furthermore, we performed additional MD simulations by restricting the rotational degrees of freedom of SO<sub>4</sub> tetrahedral units. As displayed in Figure S19, the sodium diffusion is drastically suppressed in the rigid case. This phenomenon indicates that the rotation dynamics are the main reason for sodium migration in the three cluster-based APs identified here. Thus, we can conclude that in the three identified superionic conductors, a significant correlation exists between Na migration and anion rotation in time and space, guiding the high ionic conductivities.

To further reveal the contributions of rotational dynamics to sodium migration, Figure 7a quantitatively characterizes the rotation dynamics by calculating the reorientation autocorrelation function C(t) (details are provided in Supporting Information) for SO<sub>4</sub> and SeO<sub>4</sub>; the trend of C(t) decay follows Na<sub>3</sub>BrSO<sub>4</sub> > Na<sub>3</sub>BrSeO<sub>4</sub> > Na<sub>3</sub>FSeO<sub>4</sub>, as confirmed by the flatter Helmholtz free energy surface of anion rotation in Na<sub>3</sub>BrSO<sub>4</sub> and Na<sub>3</sub>FSeO<sub>4</sub> (Figure 7b) compared to that of anions in Na<sub>3</sub>BrSeO<sub>4</sub> and Na<sub>3</sub>FSeO<sub>4</sub> (Figure S20). Thus, Na<sub>3</sub>BrSO<sub>4</sub> shows the highest ionic conductivity owing to the fastest rotational dynamics of SO<sub>4</sub>, and the limited rotational freedom of SeO<sub>4</sub> is the main reason for the low conductivity of Na<sub>3</sub>FSeO<sub>4</sub>.

However, the faster rotation dynamics of anion clusters do not always guarantee a higher ionic conductivity. As shown in Figure 7c, the C(t) between Na<sub>3</sub>BrSO<sub>4</sub> and Na<sub>3</sub>NH<sub>2</sub>Te at 700 K is directly compared, and the faster decay suggests the stronger rotational dynamics of  $NH_2$  than that of  $\widetilde{SO}_4$ , while the ionic conductivity of Na<sub>3</sub>NH<sub>2</sub>Te (206.4 mS/cm at 700 K) is lower than that of Na<sub>3</sub>BrSO<sub>4</sub> (464.4 mS/cm at 700 K, Figure 4a). Similar to the previously discussed vibrational spectra (Figure 6c), we found that overlapped low-frequency peaks of the cation vibration and anion rotation also occurred in Na<sub>3</sub>FSeO<sub>4</sub> with low anion rotational freedom at 700 K (Figure 6d). Thus, the synergy of the overlapped low-frequency peaks and significant anion rotational dynamics is necessary for a stronger coupling degree between the anion rotation and cation migration. Therefore, the local difference frequency center (LDFC, difference in averaged cation hopping frequency  $f_{\text{hopping}}$  and the averaged anion rotation frequency  $f_{\rm rotation}$ ) was calculated for evaluating the degree of coupled cation migration and anion rotation. The smallest LDFC (0.48 THz) demonstrates that the strongest coupled degree (Figure 7d, showing the LDFC of structures with obvious anion rotation and Na migration) exists in Na<sub>3</sub>BrSO<sub>4</sub>, causing the lowest activation energy and highest Na-ion conductivity. In particular, the LDFC of Na<sub>3</sub>NH<sub>2</sub>Te is 0.91 THz, suggesting a weaker coupling between the anion rotation and Na migration. Therefore, the ionic conductivity of Na<sub>3</sub>NH<sub>2</sub>Te is far lower than that of Na3BrSO4 though Na3NH2Te shows faster rotational dynamics of the anion clusters.

# 4. CONCLUSIONS

In summary, new cluster-based sodium antiperovskites are designed for solid-state electrolytes via the introduction of anion clusters and the exchange of anion ordering. By combining DFT calculations and the particle swarm optimization algorithm, we systematically studied the stability, electronic structure, and ionic conductivity. Three stable cluster-based APs (Na<sub>3</sub>BrSO<sub>4</sub>, Na<sub>3</sub>ClSO<sub>4</sub>, and Na<sub>3</sub>BrSO<sub>4</sub>) have been identified as promising solid-state electrolytes.

Among them,  $Na_3BrSO_4$  shows the highest ionic conductivity at room temperature (39.05 mS/cm), which is orders of magnitude higher than that of typical antiperovskites. The high ionic conductivity originates from the coupled cation migration and anion rotation.

This work introduces a deep understanding of anion clusters assisting cation migration, which is broadly relevant to ion conductors with anion rotation. Therefore, we expect that this work will inspire new frontiers for designing novel superionic conductors with significant anion rotation dynamics beyond the use of static structural factors. Similar strategies can also be applied to design multivalent (such as  $Mg^{2+}$  or  $Ca^{2+}$ ) ionic conductors.

## ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.4c16856.

Method for first-principles structure search and the calculation of the ionic conductivity by AIMD simulations; details about the long-lived Na-ion displacements and orientational correlation function; details about our reported local difference frequency; tolerance factors for Na<sub>3</sub>BA and Na<sub>3</sub>AB; lattice parameters and band gaps for the APs with both thermodynamical and dynamical stabilities; and the all supporting figures (PDF)

### AUTHOR INFORMATION

#### **Corresponding Author**

Hong Zhu – University of Michigan—Shanghai Jiao Tong University Joint Institute, Shanghai Jiao Tong University, Shanghai 200240, China; orcid.org/0000-0001-7919-5661; Email: hong.zhu@sjtu.edu.cn

#### Authors

- Chaohong Guan University of Michigan—Shanghai Jiao Tong University Joint Institute, Shanghai Jiao Tong University, Shanghai 200240, China
- Huirong Jing University of Michigan—Shanghai Jiao Tong University Joint Institute, Shanghai Jiao Tong University, Shanghai 200240, China
- Yu Yang University of Michigan—Shanghai Jiao Tong University Joint Institute, Shanghai Jiao Tong University, Shanghai 200240, China
- Runxin Ouyang University of Michigan—Shanghai Jiao Tong University Joint Institute, Shanghai Jiao Tong University, Shanghai 200240, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsami.4c16856

#### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was supported by National Natural Science Foundation of China (52072240, 523B2106), and the Materials Genome Initiative Center at Shanghai Jiao Tong University. All simulations were carried out with computational resources from Shanghai Jiao Tong University High Performance Computing Center.

## REFERENCES

(1) Lao, M.; Zhang, Y.; Luo, W.; Yan, Q.; Sun, W.; Dou, S. X. Alloy-Based Anode Materials toward Advanced Sodium-Ion Batteries. *Adv. Mater.* **2017**, *29* (48), No. 1700622.

(2) Kundu, D.; Talaie, E.; Duffort, V.; Nazar, L. F. The emerging chemistry of sodium ion batteries for electrochemical energy storage. *Angew. Chem., Int. Ed.* **2015**, *54* (11), 3431–3448.

(3) Kang, T.; Sun, C.; Li, Y.; Song, T.; Guan, Z.; Tong, Z.; Nan, J.; Lee, C. S. Dendrite-Free Sodium Metal Anodes Via Solid Electrolyte Interphase Engineering With a Covalent Organic Framework Separator. *Adv. Energy Mater.* **2023**, *13* (15), No. 2204083.

(4) Zhang, Z.; Roy, P. N.; Li, H.; Avdeev, M.; Nazar, L. F. Coupled Cation-Anion Dynamics Enhances Cation Mobility in Room-Temperature Superionic Solid-State Electrolytes. *J. Am. Chem. Soc.* **2019**, *141* (49), 19360–19372.

(5) Wu, E. A.; Banerjee, S.; Tang, H.; Richardson, P. M.; Doux, J. M.; Qi, J.; Zhu, Z.; Grenier, A.; Li, Y.; Zhao, E.; Deysher, G.; Sebti, E.; Nguyen, H.; Stephens, R.; Verbist, G.; Chapman, K. W.; Clement, R. J.; Banerjee, A.; Meng, Y. S.; Ong, S. P. A stable cathode-solid electrolyte composite for high-voltage, long-cycle-life solid-state sodium-ion batteries. *Nat. Commun.* **2021**, *12* (1), No. 1256.

(6) Chi, X.; Zhang, Y.; Hao, F.; Kmiec, S.; Dong, H.; Xu, R.; Zhao, K.; Ai, Q.; Terlier, T.; Wang, L. An electrochemically stable homogeneous glassy electrolyte formed at room temperature for all-solid-state sodium batteries. *Nat. Commun.* **2022**, *13* (1), No. 2854.

(7) Deng, Z.; Mishra, T. P.; Mahayoni, E.; Ma, Q.; Tieu, A. J. K.; Guillon, O.; Chotard, J.-N.; Seznec, V.; Cheetham, A. K.; Masquelier, C.; Gautam, G. S.; Canepa, P. Fundamental investigations on the sodium-ion transport properties of mixed polyanion solid-state battery electrolytes. *Nat. Commun.* **2022**, *13* (1), No. 4470.

(8) Liu, Q.; Zhao, X.; Yang, Q.; Hou, L.; Mu, D.; Tan, G.; Li, L.; Chen, R.; Wu, F. The Progress in the Electrolytes for Solid State Sodium-Ion Battery. *Adv. Mater. Technol.* 2023, 8 (7), No. 2200822.
(9) He, X.; Zhu, Y.; Mo, Y. Origin of fast ion diffusion in super-ionic conductors. *Nat. Commun.* 2017, 8, No. 15893.

(10) Wang, Y.; Richards, W. D.; Ong, S. P.; Miara, L. J.; Kim, J. C.; Mo, Y.; Ceder, G. Design principles for solid-state lithium superionic conductors. *Nat. Mater.* **2015**, *14* (10), 1026–1031.

(11) Shimoda, M.; Maegawa, M.; Yoshida, S.; Akamatsu, H.; Hayashi, K.; Gorai, P.; Ohno, S. Controlling Defects to Achieve Reproducibly High Ionic Conductivity in Na3SbS4 Solid Electrolytes. *Chem. Mater.* **2022**, *34* (12), 5634–5643.

(12) Hayashi, A.; Masuzawa, N.; Yubuchi, S.; Tsuji, F.; Hotehama, C.; Sakuda, A.; Tatsumisago, M. A sodium-ion sulfide solid electrolyte with unprecedented conductivity at room temperature. *Nat. Commun.* **2019**, *10*, No. 5266.

(13) Goodenough, J. B.; Hong, H. Y.; Kafalas, J. A. Fast Na<sup>+</sup> -ion transport in skeleton structures. *Mater. Res. Bull.* **1976**, *11*, 203–220.

(14) Hayashi, A.; Noi, K.; Sakuda, A.; Tatsumisago, M. Superionic glass-ceramic electrolytes for room temperature rechargeable sodium batteries. *Nat. Commun.* **2012**, *3*, No. 856.

(15) Wang, H.; Chen, Y.; Hood, Z. D.; Sahu, G.; Pandian, A. S.; Keum, J. K.; An, K.; Liang, C. An AirStable Na3SbS4 Superionic Conductor Prepared by a Rapid and Economic Synthetic Procedure. *Angew. Chem., Int. Ed.* **2016**, *55* (30), 8551–8555.

(16) Richards, W. D.; Tsujimura, T.; Miara, L. J.; Wang, Y.; Kim, J. C.; Ong, S. P.; Uechi, I.; Suzuki, N.; Ceder, G. Design and synthesis of the superionic conductor Na10SnP2S12. *Nat. Commun.* **2016**, *7*, No. 11009.

(17) Bron, P.; Johansson, S.; Zick, K.; Schmedt auf der Gunne, J.; Dehnen, S.; Roling, B. Li10SnP2S12: an affordable lithium superionic conductor. *J. Am. Chem. Soc.* **2013**, *135* (42), 15694–15697.

(18) Jun, K.; Sun, Y.; Xiao, Y.; Zeng, Y.; Kim, R.; Kim, H.; Miara, L. J.; Im, D.; Wang, Y.; Ceder, G. Lithium superionic conductors with corner-sharing frameworks. *Nat. Mater.* **2022**, *21*, 924–931.

(19) Zhang, Z.; L, F. N. Exploiting the paddle-wheel mechanism for the design of fast ion conductors. *Nat. Rev. Mater.* **2022**, *7*, 389–405.

(20) Zhang, Z.; Li, H.; Kaup, K.; Zhou, L.; Roy, P.-N.; Nazar, L. F. Targeting Superionic Conductivity by Turning on Anion Rotation at

Room Temperature in Fast Ion Conductors. *Matter* 2020, 2 (6), 1667–1684.

(21) Smith, J. G.; Siegel, D. J. Ion Migration Mechanisms in the Sodium Sulfide Solid Electrolyte Na3- xSb1-xWxS4. *Chem. Mater.* **2022**, 34 (9), 4166-4171.

(22) Fang, H.; Jena, P. Argyrodite-type advanced lithium conductors and transport mechanisms beyond peddle-wheel effect. *Nat. Commun.* **2022**, *13* (1), No. 2078.

(23) Yang, Y.; Xu, Z.; Guan, C.; Ouyang, R.; Jing, H.; Zhu, H. Activating paddle-wheel effect towards lower temperature in a new sodium-ion solid electrolyte, Na<sub>3.5</sub>Si<sub>0.5</sub>P<sub>0.5</sub>Se<sub>4</sub>. *J. Mater. Chem. A* **2023**, *11*, 9555–9565.

(24) Tsai, P. C.; Mair, S.; Smith, J.; Halat, D. M.; Chien, P. H.; Kim, K.; Zhang, D.; Li, Y.; Yin, L.; Liu, J.; Lapidus, S. H.; Reimer, J. A.; Balsara, N. P.; Siegel, D. J.; Chiang, Y. M. Double Paddle-Wheel Enhanced Sodium Ion Conduction in an Antiperovskite Solid Electrolyte. *Adv. Energy Mater.* **2022**, *13* (7), No. 2203284.

(25) Despotuli, A. L.; Andreeva, A. V.; Rambabu, B. Nanoionics of advanced superionic conductors. *Ionics* **2005**, *11*, 306–314.

(26) Wang, Y.; Lv, J.; Zhu, L.; Ma, Y. Crystal structure prediction via particle-swarm optimization. *Phys. Rev. B* **2010**, *82*, No. 094116.

(27) Kresse, G. J.Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **1996**, *54*, 11169–11186.

(28) Perdew, J. P.; Perdew, J. P.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(29) Giannozzi, P.; de Gironcoli, S.; Pavone, P.; Baroni, S. Ab initio calculation of phonon dispersions in semiconductors. *Phys. Rev. B* **1991**, 43, 7231–7242.

(30) Togo, A.; Tanaka, I. First principles phonon calculations in materials science. *Scr. Mater.* **2015**, *108*, 1–5.

(31) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. Hybrid functionals based on a screened Coulomb potential. *J. Chem. Phys.* 2003, 118, 8207–8215.

(32) Qi, J.; Banerjee, S.; Zuo, Y.; Chen, C.; Zhu, Z.; Holekevi Chandrappa, M. L.; Li, X.; Ong, S. P. Bridging the gap between simulated and experimental ionic conductivities in lithium superionic conductors. *Mater. Today Phys.* **2021**, *21*, No. 100463, DOI: 10.1016/j.mtphys.2021.100463.

(33) Ong, S. P.; Richards, W. D.; Jain, A.; Hautier, G.; Kocher, M.; Cholia, S.; Gunter, D.; Chevrier, V. L.; Persson, K. A.; Ceder, G. Python Materials Genomics (pymatgen): A robust, open-source python library for materials analysis. *Comput. Mater. Sci.* 2013, 68, 314–319.

(34) Novikov, I. S.; Gubaev, K.; Podryabinkin, E. V.; Shapeev, A. V. The MLIP package: moment tensor potentials with MPI and active learning. *Mach. Learn.: Sci. Technol.* **2021**, *2* (2), No. 025002.

(35) Plimpton, S. Fast Parallel Algorithms for Short-Range Molecular Dynamics. J. Comput. Phys. 1995, 117, 1–19.

(36) Xia, W.; Zhao, Y.; Zhao, F.; Adair, K.; Zhao, R.; Li, S.; Zou, R.; Zhao, Y.; Sun, X. Antiperovskite Electrolytes for Solid-State Batteries. *Chem. Rev.* **2022**, *122* (3), 3763–3819.

(37) Sun, Y.; Wang, Y.; Liang, X.; Xia, Y.; Peng, L.; Jia, H.; Li, H.; Bai, L.; Feng, J.; Jiang, H.; Xie, J. Rotational Cluster Anion Enabling Superionic Conductivity in Sodium-Rich Antiperovskite Na3OBH4. J. Am. Chem. Soc. **2019**, *141* (14), 5640–5644.

(38) Fang, H.; Jena, P. Sodium Superionic Conductors Based on Clusters. ACS Appl. Mater. Interfaces 2019, 11 (1), 963–972.

(39) Du, P. H.; Zhang, C.; Sun, J.; Li, T.; Sun, Q. Phase Stability, Strong Four-Phonon Scattering, and Low Lattice Thermal Conductivity in Superatom-Based Superionic Conductor Na3OBH4. *ACS Appl. Mater. Interfaces* **2022**, *14* (42), 47882–47891.

(40) Singh, B.; Wang, Z.; Park, S.; Gautam, G. S.; Chotard, J.-N.; Croguennec, L.; Carlier, D.; Cheetham, A. K.; Masquelier, C.; Canepa, P. A chemical map of NASICON electrode materials for sodium-ion batteries. *J. Mater. Chem. A* **2021**, *9* (1), 281–292.

(41) Lu, X.; Wang, S.; Xiao, R.; Shi, S.; Li, H.; Chen, L. Firstprinciples insight into the structural fundamental of super ionic conducting in NASICON MTi2(PO4)3 (M = Li, Na) materials for rechargeable batteries. *Nano Energy* **201**7, *41*, 626–633.

(42) Jang, S. H.; Tateyama, Y.; Jalem, R. High-Throughput Data-Driven Prediction of Stable High- Performance Na-Ion Sulfide Solid Electrolytes. *Adv. Funct. Mater.* **2022**, 32 (48), No. 2006036.

(43) Lacivita, V.; Wang, Y.; Bo, S.-H.; Ceder, G. Ab initio investigation of the stability of electrolyte/electrode interfaces in all-solid-state Na batteries. *J. Mater. Chem. A* **2019**, *7* (14), 8144–8155. (44) Xu, Z.; Duan, H.; Dou, Z.; Zheng, M.; Lin, Y.; Xia, Y.; Zhao, H.; Xia, Y. Machine learning molecular dynamics simulation

H.; Xia, Y. Machine learning molecular dynamics simulation identifying weakly negative effect of polyanion rotation on Li-ion migration. *npj Comput. Mater.* **2023**, 9 (1), 105.

(45) Zhu, Z.; Tang, H.; Qi, J.; Li, X. G.; Ong, S. P. Design Principles for Cation-Mixed Sodium Solid Electrolytes. *Adv. Energy Mater.* **2021**, *11* (7), No. 2003196.

(46) Zou, Z.; Ma, N.; Wang, A.; Ran, Y.; Song, T.; Jiao, Y.; Liu, J.; Zhou, H.; Shi, W.; He, B.; Wang, D.; Li, Y.; Avdeev, M.; Shi, S. Relationships Between Na<sup>+</sup> Distribution, Concerted Migration, and Diffusion Properties in Rhombohedral NASICON. *Adv. Energy Mater.* **2020**, *10* (30), No. 2001486.

(47) Wang, C.; Aoyagi, K.; Wisesa, P.; Mueller, T. Lithium Ion Conduction in Cathode Coating Materials from On-the-Fly Machine Learning. *Chem. Mater.* **2020**, *32*, 3741–3752.

(48) Zuo, Y.; Chen, C.; Li, X.; Deng, Z.; Chen, Y.; Behler, J.; Csanyi, G.; Shapeev, A. V.; Thompson, A. P.; Wood, M. A.; Ong, S. P. Performance and Cost Assessment of Machine Learning Interatomic Potentials. *J. Phys. Chem. A* **2020**, *124* (4), 731–745.

(49) Szymanski, N. J.; Zeng, Y.; Bennett, T.; Patil, S.; Keum, J. K.; Self, E. C.; Bai, J.; Cai, Z.; Giovine, R.; Ouyang, B.; Wang, F.; Bartel, C. J.; Clément, R. J.; Tong, W.; Nanda, J.; Ceder, G. Understanding the Fluorination of Disordered Rocksalt Cathodes through Rational Exploration of Synthesis Pathways. *Chem. Mater.* **2022**, *34*, 7015– 7028.

(50) Bartel, C. J.; Millican, S. L.; Deml, A. M.; Rumptz, J. R.; Tumas, W.; Weimer, A. W.; Lany, S.; Stevanović, V.; Musgrave, C. B.; Holder, A. M. Physical descriptor for the Gibbs energy of inorganic crystalline solids and temperature-dependent materials chemistry. *Nat. Commun.* **2018**, *9*, No. 4168.

(51) Burbano, M.; Carlier, D.; Boucher, F.; Morgan, B. J.; Salanne, M. Sparse Cyclic Excitations Explain the Low Ionic Conductivity of Stoichiometric Li7La3Zr2O12. *Phys. Rev. Lett.* **2016**, *116* (13), No. 135901.