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Structural design strategies for superionic sodium halide solid electrolytes†

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Sodium all-solid-state batteries (ASSBs) with superionic solid electrolytes (SEs) show substantial potential for large-scale energy-storage applications. Recently, lithium halide SEs have attracted attention owing to their potential compatibility with high-voltage cathode materials and high ionic conductivity. Although sodium halide SEs are believed to exhibit good electrochemical stability, very few compounds have been reported. This study provides design principles for superionic sodium halide SEs through systematic theoretical investigations of Na_3MX_6 (X = Cl, Br, and I). The Na_3MX_6 structures depend on the types and sizes of M and X: Na_3MCl_6 and Na_3MBr_6 prefer the $P\bar{3}1c$, $P2_1/n$ and $R\bar{3}$ phases, whereas Na_3Ml_6 prefers the C2/m phase. The Na_3Ml_6 C2/m phase is found to exhibit reasonably high ionic conductivity ($\sim 10^{-4}$ S cm⁻¹) and anion mixing with Br further improve Na-ion migration, leading to an even higher ionic conductivity ($\sim 10^{-3}$ S cm⁻¹) for $Na_3MBr_3l_3$. The material design principles in this study provide fundamental quidelines for the development of superionic Na halide SEs for high-voltage Na ASSBs.

Introduction

The development of next-generation batteries with high energy density and enhanced safety is required for emerging applications, such as energy storage systems (ESS) and electric vehicles.1 All-solid-state batteries (ASSBs) with solid electrolytes (SEs) are promising candidates for next-generation batteries.^{2,3} ASSBs resolve the safety concerns of conventional Li-ion batteries by replacing flammable liquid electrolytes with nonflammable inorganic SEs.4 ASSBs with SEs also enable the use of metallic anodes that exhibit significantly higher energy densities than conventional anode materials.5 Recently, various types of post-Li batteries with new cations such as Na, K, and Mg have been investigated owing to their low cost and high energy density.6-11 Among the post-Li batteries, Na-ion batteries have attracted increasing attention because of the abundance of Na.12,13 Na ASSBs have been investigated for large-scale applications, such as ESS, which require high safety. 14,15

Sulfide SEs have been widely studied for applications in Na ASSBs owing to their high ionic conductivity of 1–10 mS cm $^{-1}$ for Na₃PS₄, Na₃SbS₄ and Na₁₁Sn₂PS₁₂. ^{16–20} However, sulfide SEs

are generally unstable in moisture and exhibit a narrow electrochemical stability window. 21,22 Oxide SEs (NASICONs and β-alumina) are chemically stable and can exhibit a high ionic conductivity of \sim 1 mS cm⁻¹, but require a high-temperature sintering process to resolve the interfacial resistance. 23,24 Recently, halide SEs have been reported as promising SEs owing to their wide electrochemical stability window and compatibility with high-voltage cathode materials. $^{25-28}$ Li ternary chlorides, Li₃MCl₆, exhibit good chemical stability against high-voltage cathode materials (\sim 4 V) and have high ionic conductivity of 0.5–3 mS cm⁻¹ for Li₃YCl₆, Li₃InCl₆ and Li₃ScCl₆. $^{29-32}$

Although Na halides are expected to exhibit wide electrochemical stability,33 very few Na halide SEs, such as Na₃YCl₆, Na_3ErCl_6 , Na_2ZrCl_6 and Zr-substituted $Na_{3-x}M_{1-x}Zr_xCl_6$ (M=Yand Er)—all of which have low ionic conductivity below 10⁻⁴ S cm⁻¹—have been reported. 34-36 Owing to the ionic radius of Na (102 pm), being larger than that of Li (76 pm), Na₃MCl₆ exhibited different crystal structures of $P\bar{3}1c$, $P2_1/n$ and $R\bar{3}$ with lower ionic conductivity than the crystal structures of Li₃MCl₆, such as C2/m and $P\bar{3}m1.^{37}$ Theoretical studies predicted the phase-dependent ionic conductivities of Na₃YBr₆ and Na₃YI₆, ^{38,39} but only a few studies have reported on the phases of Na bromides and iodides, Na_3MX_6 (X = Br and I).⁴⁰ This study aims to provide guidelines for the design of novel Na halide SEs, Na_3MX_6 (X = Cl, Br and I), through systematic investigations of their structural preference, phase stability, electrochemical stability and transport properties.

This study shows that the structures of Na₃MX₆ are strongly dependent on the types and sizes of M and X. In particular, Na₃MX₆ generally exhibited $P\bar{3}1c$, $P2_1/n$, $R\bar{3}$ and C2/m phases,

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while Na₃MX₆ with relatively small M cations preferred the NaMX₄ ($P2_12_12_1$) phase.^{41,42} Na₃MCl₆ and Na₃MBr₆ preferred the $P\overline{3}1c$, $P2_1/n$ and $R\overline{3}$ phases, with the phase transitions depending on the radius of M. Na₃MI₆ preferred the C2/m phase and showed a high ionic conductivity ($\sim 10^{-4}$ S cm⁻¹). Anion mixing with Br in Na₃MI₆ further improved Na-ion migration, exhibiting a high ionic conductivity ($\sim 10^{-3}$ S cm⁻¹) that is two orders of magnitude higher than the value reported for competing Na halide SEs. The material design principles in this study offer substantial promise for the development of practical superionic Na halide SEs.

Methods

First principles calculations were performed based on the density functional theory (DFT) with a plane-wave basis set, as implemented in the Vienna Ab initio Simulation Package (VASP).43,44 The projector augmented wave method (PAW) was used for the core and valence electron interactions⁴⁵ and the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) was employed for the exchange-correlation energy functional.46 A van der Waals (vdW) density functional (optB86b-vdW) was used to address vdW interactions in layered Na halide structures. 47 An energy cutoff of 520 eV was used for the plane-wave basis sets and the k-point mesh was determined using the Python Materials Genomics (pymatgen) package, 48 including a k-point density of at least 1000 per atom. Ionic relaxations were performed until the forces were less than 0.01 eV Å^{-1} , with a convergence criterion of 10^{-5} eV for the electronic self-consistency loop.

The simulation cells of sodium halides Na_3MX_6 (X = Cl, Br and I) were generated based on the experimental structures of Na_3MX_6 that exhibited trigonal $P\bar{3}1c$ (#163), 49,50 monoclinic $P2_1/$ $n \ (\#14)^{34,35}$ trigonal $R\bar{3} \ (\#148)^{51}$ and monoclinic $C2/m \ (\#12)^{29}$ crystal structures. The trigonal P3m1 (#164) Li chloride structure, Li₃MX₆,²⁷ was also used to prepare Na₃MX₆ simulation cells. Among the possible ionic configurations for the partially occupied sites in the $R\bar{3}$, $P2_1/n$ and $P\bar{3}m1$ phases, the Na₃MX₆ structure with the lowest total energy was used for subsequent calculations. Details of the structural information of C2/m and $P\bar{3}m1$ phases are provided in Table S1.† Various metal elements in +3 oxidation states have been considered for ternary metal halides, Na₃MX₆, including group 3 elements (Sc, Lu and Y), group 13 elements (Al, Ga, In and Tl), group 15 elements (Bi) and lanthanides (Yb, Tm, Er, Ho, Dy, Tb, Gd, Sm, Nd and La). The transition metals with multiple oxidation states were excluded in this study. The phase stability of Na_3MX_6 (X = Cl, Br and I) was evaluated by calculating the decomposition energy, $E_{\rm d}$, against the competing stable phases NaX and MX₃. The metastable Na₃MX₆ phase with an E_d below 25 meV per atom was considered to be a stable phase, owing to stabilization by entropic effects and kinetic inhibition. Further experimental studies can be performed to identify the stable structure of Na₃MX₆, based on the theoretical works.

The Na-ion potential energy landscape in Na₃MX₆ was obtained using the bond-valence site energy (BVSE) method, as implemented in SoftBV software.⁵² The potential energy of the

Na sites was calculated using the Morse-type interaction potential with a grid density of 0.1 Å. The Na-ion migration path was predicted using the isosurface of the Na-ion probability density and the minimum energy value between the migration paths for the Na-ion migration energy barrier was obtained. Naion diffusivity in Na₃MX₆ was examined using ab initio molecular dynamics (AIMD) simulations with an energy cutoff of 350 eV, Γ -point-only k-point grid and the NVT ensemble with a Nosé-Hoover thermostat. A 2 imes 2 imes 1 supercell was used for $P\bar{3}1c$, $P2_1/n$ and $R\bar{3}$, and a 2 × 1 × 2 supercell was used for the C2/m structure for the AIMD calculations corresponding to 80 atoms for the $P\bar{3}31c$, $P2_1/n$ and C2/m, and 120 atoms for $R\bar{3}$ structures. The Na-ion diffusivity was evaluated using the mean squared displacement (MSD) at five different temperatures (700, 750, 800, 900 and 1000 K) for a window of 100 to 200 ps, with a time step of 2 fs. Data from the AIMD simulations were analyzed using the diffusion analysis module of the pymatgen package.48 The total mean squared displacement (TMSD) and effective ion jumps were calculated to evaluate the relative standard deviation of diffusivity based on previous studies. 53,54 The diffusion coefficient, D, was derived using the TMSD of Na ions as a function of the time interval, Δt :

$$D = \frac{1}{2d\Delta t} \frac{\text{TMSD}(\Delta t)}{n} = \frac{1}{2d\Delta t n} \sum_{i=1}^{n} \frac{1}{N_{\Delta t}} \sum_{t=0}^{t_{\text{tot}} - \Delta t} |r_i(t + \Delta t) - r_i(t)|^2$$
(1)

where d is the dimensionality, n is the total number of Na ions, $N_{\Delta t}$ is the total number of time intervals and r_i is the Na ion trajectory. The ionic conductivity, σ , was calculated using the Nernst-Einstein equation:

$$\sigma = \frac{(ze)^2 cD}{k_{\rm B}T} \tag{2}$$

where z is the valence of the ion, e is the elementary charge, e is the concentration of the ion, e is the diffusion coefficient, e is the Boltzmann constant and e is the temperature. Na-ion migration trajectories during the AIMD simulations were observed using a 25 \times 25 \times 25 grid mesh. Isosurfaces of the ionic probability densities were obtained to visualize ion migration using the mean ionic probability density e0.

The electrochemical stability of Na_3MX_6 (X = Cl, Br and I) was investigated using the Materials Project (MP) database. The grand potential phase diagram as a function of the chemical potential of Na was obtained using the pymatgen package to evaluate the electrochemical stability window of Na_3MX_6 . The total energies of Na_3MX_6 were updated using equivalent settings in the MP for the calculations. The oxidation and reduction potentials with their phase equilibria were examined to determine the electrochemical stability of Na_3MX_6 . Na_3MX_6 compounds that were unstable against phase decomposition were excluded from the electrochemical stability calculations.

Results

The most stable structure of Na₃MX₆ (X = Cl, Br and I) among trigonal $P\bar{3}1c$, monoclinic $P2_1/n$, trigonal $R\bar{3}$, monoclinic C2/m

and trigonal $P\bar{3}m1$ was determined by comparing the total energies of the phases, as shown in Fig. S1-S3 and Table S2.† Although the energy differences among the phases are small and several phases can be considered as the most stable phase, there exists a general trend for phase transitions among the structures, as a function of the size of cation (M) and anion (X). The phase preference for Na₃MCl₆ agrees with a previous work³⁷ showing that Na₃MCl₆ with relatively small M cations prefers the trigonal P31c phase, whereas Na₃MCl₆ with modestly large M cations prefers the monoclinic $P2_1/n$ phase and Na_3MCl_6 with even larger M cations above 90 pm prefers the $R\bar{3}$ phase, as shown in Fig. S1.† The phase preference of Na₃MBr₆ was found to be comparable to that of Na₃MCl₆ in the $P\bar{3}1c$, $P2_1/2$ n and $R\bar{3}$ phases; however, the driving force for the phase transitions to $P2_1/n$ and $R\overline{3}$ for Na₃MBr₆ was relatively weaker than for Na₃MCl₆, as shown in Fig. S1.† Therefore, phase transitions (from $P\bar{3}1c$ to $P2_1/n$ and from $P2_1/n$ to $R\bar{3}$) require relatively larger M cations in Na₃MBr₆ compared with Na₃MCl₆. Na_3MCl_6 and Na_3MBr_6 preferred $P\bar{3}1c$, $P2_1/n$ and $R\bar{3}$ phases, while Na_3MI_6 preferentially exhibited the C2/m phase over the other phases. The energy difference plot in Fig. S2† shows this phase preference of C2/m compared with other phases for Na₃MI₆. The energy differences for the $P\bar{3}1c$, $P2_1/n$, $R\bar{3}$, C2/m and $P\bar{3}m1$ phases for Na₃MX₆ (X = Cl, Br and I) are listed in Table S2.† The energy difference among the phases was negligible for Na₃MBr₆ since they were in the phase transition region. The ground state of structure with the lowest energy should be examined to obtain the accurate results.

The phase stability of Na_3MX_6 (X = Cl, Br and I) was evaluated using the decomposition energy, $E_{\rm d}$, against the competing stable phases, NaX and MX₃. The most stable phase of MX₃ among the experimental structures listed in Tables S3 and S4† was used to evaluate E_d . The E_d values for the $P\bar{3}1c$, $P2_1/n$, $R\bar{3}$, C2/m and $P\bar{3}m1$ structures are illustrated as a heat map in Fig. S3 and S4.† Na₃MX₆ phases with negative E_d values (dark blue) were considered stable against decomposition to NaX and MX_3 , whereas Na_3MX_6 phases with positive E_d values under 25 meV per atom were considered metastable phases owing to the entropic effects and kinetic barrier of decomposition. Na₃MX₆ phases with positive E_d values above 25 meV per atom (light brown) were considered unstable phases, which generally included large M cations (M_{radii} > 95 pm), such as Sm, Nd and La. Na₃MCl₆ typically exhibit stable phases, whereas most Na₃MBr₆ and Na₃MI₆ exhibit metastable or unstable phases. The Na₃MI₆ E_d values are higher than those for Na₃MBr₆, suggesting that the relatively large X in Na₃MX₆ decreases phase stability. The most stable Na_3MX_6 phases with the lowest E_d value among the $P\bar{3}1c$, $P2_1/n$, $R\bar{3}$, C2/m and $P\bar{3}m1$ phases are shown in Fig. 1(a) and Tables S5 and S6.†

The Na₃MX₆ structures are strongly dependent on the sizes of M and X. The octahedral factor, t, was employed to investigate the structural preferences of Na₃MX₆. Defined as the ratio of the radius of cation to anion (r^+/r^-) , this octahedral factor between M and X $(t_{MX} = r_{M}/r_{X})$ effectively described the structure of the Li-M-X compound in an earlier study. 25,56 Li-M-X was found to form MX_8 cubes for high values of t_{MX} , such as fluorides, while the structures changed to MX6 octahedra for

lower values of $t_{\rm MX}$, such as chlorides (Li₃MCl₆). The Li-M-X compound exhibited an MX4 tetrahedron upon further decrease in $t_{\rm MX}$, forming LiMX₄. ^{25,56} The M-X structural changes in the Na-M-X compounds were consistent with these prior results for the Li-M-X compounds, suggesting that moderate values of $t_{\rm MX}$ result in Na₃MX₆ phases, whereas lower values of t_{MX} result in NaMX₄ phases. Na-M-X compounds with relatively small cations, such as Al and Ga, showed low t_{MX} values, exhibiting the NaMX₄ (P2₁2₁2₁) phase instead of the Na₃MX₆ phase, as shown in Table S7.†

The octahedral factor between A and X ($t_{AX} = r_A/r_X$, A = Li and Na) and t_{MX} was evaluated to investigate the structure of Na₃MX₆ in Fig. 1(b-d). Using the t_{AX} and t_{MX} as x and y values in the two-dimensional plot in Fig. 1(b), the structural preferences of A₃MX₆ among the $P\bar{3}1c$, $P2_1/n$, $R\bar{3}$, C2/m and $P\bar{3}m1$ phases were assessed. Data that lie on the dashed line in Fig. 1(b) feature t_{AX} that is equivalent to t_{MX} , indicating that the sizes of octahedra of MX₆ and AX₆ are comparable (e.g., Li₃ScCl₆). Data points for A₃MX₆ lie above or below this dashed line when the size of M is larger or smaller than A, respectively. Na₃MX₆ (X =Cl, Br and I) is positioned below the dashed line because the ionic radius of Na (102 pm) is typically larger than that of the M cations. Most Li chlorides and bromides, Li_3MX_6 (X = Cl and Br), were found to lie above the dashed line because of the smaller ionic radius of Li (76 pm) compared with that of the M cations. Li fluorides and iodides (Li₃MX₆, X = F and I) were disregarded in this plot because they exceeded the span of t for Na_3MX_6 , exhibiting high values of t_{MX} above 0.6 for Li_3MF_6 and low values of t_{AX} under 0.35 for Li₃MI₆.

In Fig. 1(b), the NaMX₄ $(P2_12_12_1)$ phase for relatively small M cations with low values of $t_{\rm MX}$ in Table S7† is represented in yellow. For Na_3MX_6 with higher values of t_{MX} than those of NaMX₄, the most stable structural phase among $P\bar{3}1c$, $P2_1/n$, $R\bar{3}$, C2/m and $P\bar{3}m1$ is represented by black, red, blue, green and purple, respectively. Li_3MX_6 compounds (X = Cl and Br) generally exhibited the C2/m phase, whereas the $P\bar{3}m1$ phase was the stable phase for Li₃MCl₆ with large M cations, corresponding to a high $t_{\rm MX}$ above 0.5.57 Na₃MI₆ showed similar values of t_{AX} and t_{MX} ($t_{AX} \sim 0.45$ and $0.35 < t_{MX} < 0.5$) to Li₃MCl₆, resulting in a preference for the C2/m phase. As the size of the X anion increases ($t_{AX} > 0.5$), Na₃MX₆ (X = Cl and Br) was found to prefer the $P\bar{3}1c$, $P2_1/n$ and $P\bar{3}$ phases to the C2/m phase, with $P\bar{3}1c$ - $P2_1/n$ - $R\bar{3}$ phase transitions occurring for Na₃MX₆ (X = Cl and Br) with increased size of M (i.e., with larger t_{MX}).

The phase preferences of A_3MX_6 (A = Li and Na; X = Cl, Br and I) with M in the p-block (groups 13 and 15; M = Al, Ga, In, Tl and Bi) was observed to be slightly different, with phase transitions (from $P2_12_12_1$ to C2/m, from $P2_12_12_1$ to $P\bar{3}1c$, from $P\bar{3}1c$ to $P2_1/n$) occurring with relatively large M cations. For example, the group 3 element Sc (75 pm) exhibited phase transitions from $P2_12_12_1$ to $P\overline{3}1c$ for Na_3ScI_6 and from $P\overline{3}1c$ to $P2_1/n$ for Na₃ScCl₆, whereas the group 13 element In, with a relatively large ionic radius (80 pm), exhibited $P2_12_12_1$ for NaInI₄ and $P\overline{3}1c$ for Na₃InCl₆. The difference in electronegativity between M and X is smaller for the p-block elements than for the d- and f-block elements (i.e., group 3 elements and lanthanides), resulting in weaker Coulomb interactions and different phase-transition

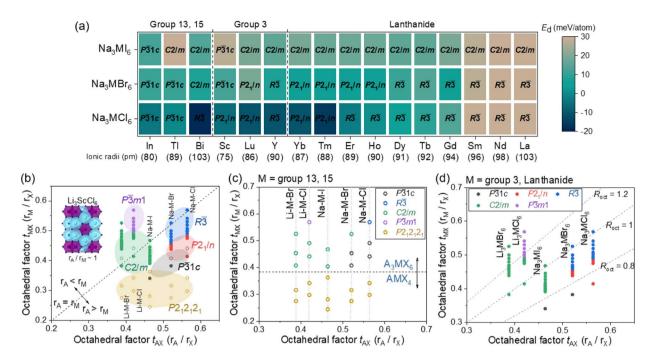


Fig. 1 (a) Heat map for the decomposition energy (E_d) of Na halides (Na₃MX₆, X = Cl, Br and I) against the competing phases NaX and MX₃. The most stable phase for the crystal structures of $P\bar{3}1c$, $P2_1/n$, $R\bar{3}$, C2/m and $P\bar{3}m1$ was used to evaluate E_d for Na_3MX_6 . (b-d) Structural preference tendencies of the crystal systems for $P\bar{3}1c$, $P2_1/n$, $R\bar{3}$, C2/m, $P\bar{3}m1$ and $P2_12_12_1$ as a function of the octahedral factors for AX_6 (r_A/r_X) and AX_6 (r_A r_{χ}) for Li and Na metal ternary halides based on M elements: (b) all elements, (c) group 13 and 15 elements, (d) group 3 and lanthanide elements. Compounds in same composition group (A-M-X) are aligned vertically in (b-d). $R_{\rm oct}$ in (d) corresponds to the ratio of $r_{\rm A}$ to $r_{\rm M}$.

trends.⁵⁷ Hence, the phase transitions of A₃MX₆ with p-block elements occurred only with a relatively large M, for which the difference in electronegativity becomes appreciable. The data for A₃MX₆ with p-block elements are presented using open symbols in Fig. 1(b and c) and the phase preferences of A₃MX₆ in Fig. 1(b) are divided into two plots based on the M cation: Fig. 1(c) for group 13 and 15 elements and Fig. 1(d) for group 3 and lanthanide elements.

Fig. 1(c) shows the preference of the MX₄ tetrahedron for relatively small p-block elements with low values of $t_{\rm MX}$ (<0.38), forming the NaMX₄ $(P2_12_12_1)$ phase. Because this $P2_12_12_1$ phase includes MX4 tetrahedron showing low ionic conductivity,26 M cations with small ionic radii may be neglected in the design of superionic Na-M-X SEs. The phase preference of A₃MX₆ for group 3 elements and lanthanides with relatively large ionic radii (>74 pm) is shown in Fig. 1(d). Here, the ratio of octahedral factors, $R_{\text{oct}} = t_{\text{MX}}/t_{\text{AX}} = r_{\text{M}}/r_{\text{A}}$ was used to classify the A₃MX₆ phases. The value of $R_{\rm oct}$ is higher or lower than 1 when the cation M is larger or smaller than A, respectively. The R_{oct} values were generally 1.0-1.3 for Li₃MCl₆ and they exhibited a phase transition from C2/m to $P\bar{3}m1$ at a $R_{\rm oct}$ value of approximately 1.2. The R_{oct} values were generally 0.8–1.0 for Na₃MX₆ (X = Cl, Br and I) because of the large ionic radius of Na (102 pm). Na₃MI₆ maintained the C2/m phase in this range, whereas Na₃MBr₆ and Na₃MCl₆ exhibited a phase transition from $P2_1/n$ to $R\overline{3}$ phase at $R_{\rm oct}$ values of approximately 0.85.

The Na-ion potential energy landscapes for the $P\bar{3}1c$, $P2_1/n$ and $R\bar{3}$ phases of Na₃MX₆ (Cl and Br) and the C2/m phase of Na₃MI₆ were predicted using the BVSE method. The experimental structures of Na₃InCl₆, Na₃ErCl₆, Na₃GdCl₆ and Na_3GdI_6 were used to examine Na-ion migration in the $P\bar{3}1c$, $P2_1/n$, $R\bar{3}$ and C2/m phases, respectively. The isosurface of the Na-site energy (light blue) was obtained to visualize the Na-ion migration pathways, as shown in Fig. 2 and S5-S9.† The calculation results indicate that the trigonal $P\bar{3}1c$ and $R\bar{3}$ phases of Na₃MCl₆ show 1D paths between octahedral sites (Oct.-Oct.) along the z-axis as well as 3D paths between octahedral sites via tetrahedral interstitial sites (Oct.-Tet.-Oct.). The monoclinic $P2_1/n$ phase of Na₃MCl₆ exhibits 3D paths between octahedral and prism sites (Oct.-Prism) and between octahedral and prism sites via tetrahedral interstitial sites (Oct.-Tet.-Prism), agreeing with previous studies.37 The Na-ion migration paths in Na₃InBr₆ $(P\bar{3}1c)$, Na₃ErBr₆ $(P2_1/n)$ and Na₃GdBr₆ $(R\bar{3})$ were found to be consistent with the paths in Na₃MCl₆, as shown in Fig. 2, while the energy barrier between the migration paths was slightly decreased compared to Na₃MCl₆ (Fig. S5†). The Na-ion migration paths in Na₃GdI₆ for the C2/m phase include threedimensional paths between octahedral sites connected by tetrahedral interstitial sites (Oct.-Tet.-Oct.). Details of the migration paths in Na₃InBr₆ ($P\bar{3}1c$), Na₃ErBr₆ ($P2_1/n$), Na₃GdBr₆ $(R\bar{3})$ and Na₃GdI₆ (C2/m) are presented in Fig. S6-S9,† respectively.

The Na-ion migration energy barriers (E_a) in the $P\bar{3}1c$, $P2_1/n$ and $R\bar{3}$ phases of Na₃MX₆ (M = In, Er, Gd; X = Cl, Br) and the C2/m phase of Na₃GdI₆ were predicted using BVSE, as shown in Fig. 2 and S5.† The trigonal $P\bar{3}1c$ and $R\bar{3}$ phases of Na₃MCl₆ exhibited E_a of 0.45 and 0.35 eV, respectively, for the 1D paths between face sharing octahedral sites (Na1-i1), and E_a of 0.53

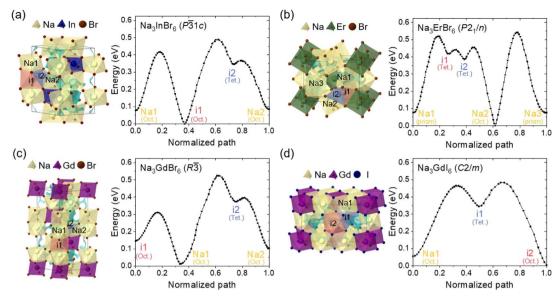


Fig. 2 Na-ion potential energy landscape of (a) Na₃lnBr₆ (trigonal $P\overline{3}1c$), (b) Na₃ErBr₆ (monoclinic $P2_1/n$), (c) Na₃GdBr₆ (trigonal $R\overline{3}$) and (d) Na₃Gdl₆ (monoclinic C2/m) calculated using the BVSE method, including Na-ion migration energy barriers along the migration paths. Details of migration paths are shown in Fig. S6-S9.†

and 0.65 eV, respectively, for the 3D paths between octahedral sites through the interstitial tetrahedral site (i1-i2-Na2 and Na1-i2-Na2). Note that E_a for the 3D paths is the key determiner for long-range migration rates. The E_a values in the $P2_1/n$ phase of Na₃MCl₆ were 0.60 eV for migration paths between octahedral and prism sites through tetrahedral interstitial sites (Na1i1-i2-Na2) and 0.70 eV for the migration paths between octahedral and prism sites (Na2-Na3). The higher values of Ea for the $R\bar{3}$ and $P2_1/n$ phases indicate that the Na-ion diffusivity would be reduced for those phases. The $P\bar{3}1c$, $P2_1/n$ and $R\bar{3}$ phases of Na₃MBr₆ exhibited slightly lower E_a than those of Na_3MCl_6 as shown in Fig. 2. The E_a for the 3D paths in the $P\bar{3}1c$, $P2_1/n$ and $R\bar{3}$ phases of Na₃MBr₆ were 0.49, 0.54 and 0.52 eV, respectively, suggesting an improvement in Na-ion migration in Na_3MBr_6 . The E_a value for the C2/m phase of Na_3GdI_6 was computed as 0.48 eV for the 3D paths between octahedral sites through the interstitial tetrahedral sites (Na1-i1-i2), indicating that Na-ion diffusivity in the C2/m phase would be higher than in other phases. The E_a value for the 1D and 3D paths of Na₃MX₆ (M = In, Er, Gd; X = Cl, Br) and Na₃GdI₆ are listed in Table S8.†

In addition to simple empirical BVSE calculations, 58,59 further detailed analysis of Na-ion migration in the $P\bar{3}1c$, $P2_1/n$ and $R\bar{3}$ phases of Na₃MX₆ (X = Br and I) were performed using AIMD simulations. The Na-ion diffusivity in Na₃InBr₆ ($P\bar{3}1c$), Na_3ErBr_6 ($P2_1/n$), Na_3GdBr_6 ($R\overline{3}$), Na_3YI_6 (C2/m) and Na_3GdI_6 (C2/m) were evaluated using the Na-ion mean squared displacement (MSD), as shown in Fig. S10.† Na₃ErBr₆ (P2₁/n) showed negligible Na-ion MSD over 100 ps at 900 K (Fig. S11†), suggesting the low ionic conductivity of Na₃MBr₆ with P2₁/n structure. According to earlier studies, the ionic conductivity of Na₃ErBr₆ should be approximately 10⁻⁹ S cm⁻¹, reflecting the fact that inter-site hopping was not observed in the MSD plot at 900 K.60 The Na-ion diffusivities of Na₃MBr₆ were improved in the $P\bar{3}1c$ and $R\bar{3}$ phases, and $P\bar{3}1c$ showed the highest diffusivity among the $P\bar{3}1c$, $P2_1/n$ and $R\bar{3}$ phases of Na₃MBr₆. Note that, in Fig. 3(a), the Na-ion diffusivities of Na₃InBr₆ ($P\bar{3}1c$) at 900 and 1000 K (open triangles) are extrapolated values from the lowertemperature simulations because Na₃InBr₆ melted at high temperature.

As shown in Fig. 3(b), Na₃GdBr₆ (R3) exhibited activation energy of 0.50 eV and ionic conductivity of $1.2 \times 10^{-6} \,\mathrm{S\,cm^{-1}}$ at room temperature. Na-ion MSD was found to further improve in Na₃InBr₆ (P31c), exhibiting activation energy of 0.37 eV and ionic conductivity of $5.8 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature. The C2/m phase of Na₃MI₆ showed lower activation energy and higher ionic conductivity compared with the $P\bar{3}1c$ and $R\bar{3}$ phases of Na₃MBr₆. Na₃GdI₆ and Na₃YI₆ exhibited activation energies of 0.30 and 0.34 eV and ionic conductivities of 5.9×10^{-4} and $2.4 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature, respectively. The activation energies, ionic conductivities and error bounds are listed in Tables 1 and S9.† The activation energy and Na ionic conductivity of the C2/m phase of Na₃YI₆ showed good agreement with previous theoretical work39 reporting 0.32 eV and 3.5 \times 10⁻⁴ S cm⁻¹, respectively. In the earlier study, the high ionic conductivity of C2/m phase was predicted for Na₃YCl₆ and Na_3YBr_6 , ³⁸ but $P2_1/n$ phase was favorable structure for Na_3YCl_6 , exhibiting low ionic conductivity approximately 10^{-9} S cm⁻¹.35

The isosurfaces of the Na-ion probability densities were plotted using an isosurface value of $2P_0$ for Na₃InBr₆ ($P\bar{3}1c$), Na_3GdBr_6 ($R\bar{3}$) and Na_3GdI_6 (C2/m) in Fig. 3(c-e), respectively, based on the Na-ion trajectories during 50 ps AIMD simulations at 800 K. As predicted from the relatively low values of E_a for the 1D paths in the $P\bar{3}1c$ and $R\bar{3}$ phases (Fig. 2), Na-ion isosurfaces were more connected for 1D paths along the z-axis, as shown in Fig. 3(c and d), S12 and S13.† The higher E_a for the 3D paths in $R\bar{3}$ phases inhibited long-range diffusion along the xy plane,

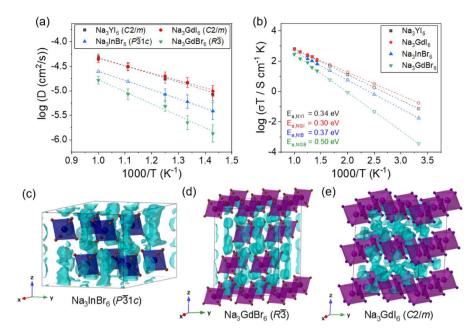


Fig. 3 Arrhenius plots of Na-ion (a) diffusivity and (b) conductivity for Na_3lnBr_6 , Na_3GdBr_6 , Na_3GdBr_6 , Na_3Gdl_6 . The open symbols in (a) and (b) correspond to the ionic conductivities obtained by extrapolating from low- and high-temperature data, respectively. (c-e) Isosurfaces of the Na-ion probability densities (light blue) from 50 ps AIMD calculations at 800 K, plotted using an isosurface value of $2P_0$ for (c) Na_3lnBr_6 , (d) Na_3GdBr_6 and (e) Na_3Gdl_6 , where P_0 is mean ionic probability density. The octahedra in (c-e) correspond to $lnBr_6$, $lnBr_6$ and $lnBr_6$

Table 1 Na ionic conductivities and activation energies of superionic Na halide SEs

Composition	Structure	σ at 300 K (mS cm ⁻¹)	$E_{\rm a}$ (eV)
Na ₃ InBr ₆	P31c	0.058	0.37
Na ₃ ErBr ₆	$P2_1/n$	10^{-6}	N/A
Na ₃ GdBr ₆	$R\bar{3}$	0.0012	0.50
Na ₃ YI ₆	C2/m	0.24	0.34
Na ₃ YI ₆ (ref. 39)	C2/m	0.35	0.32
Na ₃ GdI ₆	C2/m	0.59	0.30
Na ₃ YBr ₃ I ₃	C2/m	3.3	0.25
Na ₃ GdBr ₃ I ₃	C2/m	7.5	0.21

resulting in the low ionic conductivity of $R\bar{3}$. The Na-ion diffusivity increased in the $P\bar{3}1c$ phase for Na₃MBr₆ as diffusion along the 3D paths is facilitated in this phase, as shown in Fig. S12.† In Fig. 3(e) and S14,† it can be seen that the isosurfaces in Na₃GdI₆ are well connected through the 3D paths, verifying the high diffusivity in the C2/m phase.

Anion mixing was performed to increase the ionic conductivity of the C2/m phase Na_3MI_6 , based on previous studies showing that Cl–Br mixing enhanced the ionic conductivity of Li_3MCl_6 owing to the increase in disorder in chemical bonding. 57,61,62 $Na_3MBr_xI_{6-x}$ (M=Y) and Gd) structures with the lowest energy among 100 randomly generated simulation cells were used for the calculations. The phase stability of $Na_3-MBr_xI_{6-x}$ was examined using the decomposition energy, E_d , as shown in Table S10.† $Na_3MBr_xI_{6-x}$ was found to be a metastable phase and it showed a phase transition from C2/m to $R\bar{3}$ as the ratio of Br in $Na_3MBr_xI_{6-x}$ increased (x > 3).

The Na-ion diffusivity and conductivity of the C2/m phase in Na₃MBr₃I₃ (M = Y and Gd) were evaluated using AIMD simulations, as shown in Fig. 4. The Arrhenius plot of the Na-ion diffusivity in Fig. 4(a) was obtained using the Na-ion MSD (Fig. S15†). Na₃YBr₃I₃ and Na₃GdBr₃I₃ exhibited activation energies of 0.25 and 0.21 eV and ionic conductivities of 3.3 imes 10^{-3} and 7.5×10^{-3} S cm⁻¹ at room temperature, respectively. Anion mixing with Br in the C2/m phase of Na₃MI₆ was found to be a valuable strategy to enhance the ionic conductivity. The predicted ionic conductivity of Na₃GdBr₃I₃ (7.5 mS cm⁻¹) is the highest value among the studied Na halide SEs. The activation energies, ionic conductivities and error bounds for Na₃YBr₃I₃ and Na₃GdBr₃I₃ are listed in Tables 1 and S11.† The isosurfaces of the ionic probability densities for Na₃GdI₆ and Na₃GdBr₃I₃ are presented in Fig. 4(c) using an isosurface value of $2P_0$ based on the Na-ion trajectories from 50 ps AIMD simulations at 800 K. The ionic probability densities for Na, Br and I are shown in light blue, orange and blue, respectively. The isosurfaces of the Na-ion probability densities for Na₃GdBr₃I₃ were found to be more connected through the 3D paths than those for Na₃GdI₆, confirming the higher Na-ion diffusivity in Na₃GdBr₃I₃. Anion mixing likely increases disorder in the chemical bonding and enlarges the vibration of Br and I anions in the crystal lattice, which facilitates Na-ion migration. The isosurfaces of the ionic probability densities with views along various directions are shown in Fig. S16 and S17.†

The electrochemical stability window of Na_3MX_6 (X = Cl, Br and I) was evaluated using a grand potential diagram as a function of the chemical potential of Na. As shown in Fig. 5, Na_3MCl_6 and Na_3MBr_6 display high oxidation potential of approximately 3.9 and 3.7 V, respectively, suggesting good

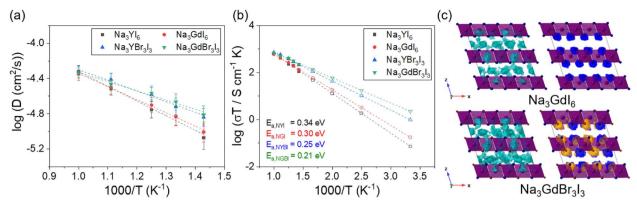


Fig. 4 Arrhenius plots of Na-ion (a) diffusivity and (b) conductivity for Na₃Yl₆, Na₃Gdl₆, Na₃Gdl₇ and Na₃GdBr₃l₃. The open symbols in (b) correspond to the ionic conductivities obtained by extrapolating from high-temperature data. (c) Isosurfaces of the ionic probability densities for Na, Br and I (light blue, orange and blue, respectively) from 50 ps AIMD calculations at 800 K, plotted using an isosurface value of $2P_0$ for Na₃GdI₆ and Na₃GdBr₃I₃. The octahedra in (c) correspond to GdBr_xI_{6-x}.

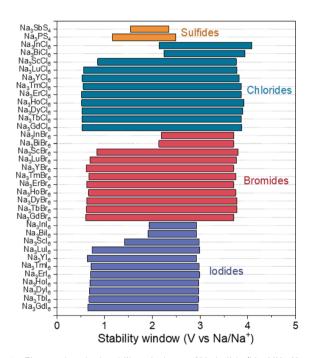


Fig. 5 Electrochemical stability windows of Na halide (Na_3MX_6 , X = Cl, Br and I) and sulfide (Na₃PS₄ and Na₃SbS₄) SEs.

electrochemical stability against oxidation at high voltages. We point out that, under real conditions, oxidation reactions typically occur at potentials higher than these theoretical limits owing to the kinetic barrier for the phase decomposition reaction and the presence of protective decomposition layers at the interface. Therefore, Na₃MCl₆ and Na₃MBr₆ could be applied to ASSBs with high-voltage cathodes and they show substantial advantages compared with sulfide SEs with low oxidation potentials (<2.5 V), such as Na₃PS₄ and Na₃SbS₄.⁶³ Na₃MI₆ exhibits an oxidation potential of approximately 3.0 V, suggesting lower electrochemical stability against oxidation than Na₃MCl₆ and Na₃MBr₆. Again, kinetic reaction barriers and decomposition layers may help to prevent the oxidation

reaction. Interface coatings could be applied to passivate the oxidative decomposition of Na₃MI₆.33

The reduction potentials of Na_3MX_6 (X = Cl, Br and I) were found to depend on the identity of the M element, agreeing with previous studies on Li halides Li₃MX₆ that electronegativity difference between M and X affected electrochemical stabilities.⁵⁷ Stronger electron localization between M and X would decrease the reduction potential. The reduction potentials of Na₃MX₆ with p-block elements are approximately 2.1 V, whereas Na₃MX₆ with group 3 elements and lanthanides exhibit a much lower reduction potential of approximately 0.6 V. Overall, however, the Na₃MX₆ compounds generally show a wide electrochemical window. Reductive decomposition resulted in the formation of metallic compounds, as shown in Table S12,† enabling continuous reduction reactions of Na₃MX₆ by conducting electrons.64 Therefore, we suggest that interfacial coatings between the Na metal anode and Na₃MX₆ would be required to inhibit the continuous reductive decomposition of Na₃MX. The oxidation and reduction potentials of Na₃MX₆ and the phase equilibria at these potentials are summarized in Table S12.†

Conclusions

In this study, we have provided design principles of superionic Na halide SEs through systematic analyses of the structural preference, phase stability, electrochemical stability and transport properties of Na_3MX_6 (X = Cl, Br and I). The structures of Na₃MX₆ are strongly dependent on the types and sizes of cations M and anions X, and the octahedral factors were found to be effective descriptors for predicting the stable phases of Na_3MX_6 . Na_3MX_6 generally exhibits $P\overline{3}1c$, $P2_1/n$, $R\overline{3}$ and C2/mphases, while Na₃MX₆ with relatively small M cations exhibits the NaMX₄ $(P2_12_12_1)$ phase. Na₃MCl₆ and Na₃MBr₆ prefer the $P\bar{3}1c$, $P2_1/n$ and $P\bar{3}$ phases and phase transitions from $P\bar{3}1c$ – $P2_1/n$ $n-R\bar{3}$ were found to occur with increasing size of M. Na₃MI₆ showed octahedral factor values similar to those of the C2/m phase of Li₃MCl₆, indicating a preference for the C2/m phase

over the $P\bar{3}1c$, $P2_1/n$ and $P\bar{3}$ phases. The effects of the structures of Na₂MX₆ on Na-ion migration were investigated using the BVSE method and AIMD simulations. The energy barriers of Naion migration in the $R\bar{3}$ and $P2_1/n$ phases were found to be higher than those in the $P\bar{3}1c$ phase for Na₃MCl₆ and Na₃MBr₆, whereas the C2/m phase Na₃MI₆ showed a lower barrier than the other phases. AIMD simulations likewise revealed that the $P\bar{3}1c$ phase exhibits high ionic conductivity ($\sim 10^{-5} \, \mathrm{S \, cm}^{-1}$) relative to the other phases of Na₃MBr₆ and that the C2/m phase of Na₃MI₆ shows even higher ionic conductivity ($\sim 10^{-4} \text{ S cm}^{-1}$). Anion mixing with Br in Na₃MI₆ further enhanced Na-ion migration, resulting in a superb ionic conductivity of $7.5 \times 10^{-3} \, \mathrm{S \, cm^{-1}}$ for Na₃GdBr₃I₃, which is the highest value among the reported Na halide SEs. Na₃MCl₆ and Na₃MBr₆ exhibit natively high oxidation potentials, enabling compatibility with high-voltage cathodes (~4 V), whereas interfacial coatings would be required to use Na₃MI₆ with high-voltage cathodes. The material design principles in this work provide fundamental guidelines for the development of superionic Na halide SEs for high-voltage Na

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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