



Cite this: DOI: 10.1039/d6ta05828k

Deconvoluting fast ion conduction in glassy antiperovskite $\text{Li}_2\text{OHBr}_{0.5}\text{Cl}_{0.5}$ via machine-learning potentials: lattice compliance and the partial paddlewheel mechanism

Ram Sewak * and Anirban Mondal *

Harnessing structural amorphization in mixed-halide antiperovskites offers a promising route to designing next-generation superionic solid electrolytes, yet the underlying multiscale transport physics remains elusive due to the timescale limitations of *ab initio* methods. In this work, we develop a highly accurate and transferable deep neural network interatomic (DNN) potential within the DP-GEN active-learning framework to explore lithium-ion dynamics in glassy $\text{Li}_2\text{OHBr}_{0.5}\text{Cl}_{0.5}$ over extended timescales. Temperature-dependent simulations reveal a highly heterogeneous potential energy landscape in which a dense population of distortion-induced metastable interstitial sites coexists with parent-topology-associated environments, establishing a continuous percolation network with a broad continuum of migration barriers. The population of these dynamically accessible coordination environments maximizes near 500 K, capturing a peak in configurational heterogeneity that closely echoes experimental glass-transition behavior. Vibrational analysis shows that chemical substitution with the more polarizable Br^- anion induces structural lattice softening, diluting framework restoring forces and dynamically widening transport bottlenecks. Crucially, concurrent event-based tracking and localized conditional autocorrelation modeling expose a powerful temporal association between polyanionic OH^- rotational fluctuations and successful Li^+ translational jumps. However, a severe mismatch in absolute frequencies and activation barriers rules out a classical, fully synchronized “paddlewheel” mechanism. Instead, we show that lithium transport is driven by independent, thermally activated hops, locally facilitated and smoothed by high-frequency librations and moderate-angle hydroxyl reorientations. By delivering a unified atomistic picture of how topological disorder, lattice softening, and partially coupled polyanionic dynamics synergistically accelerate cation conduction, this work provides vital mechanistic design principles for the rational engineering of superionic amorphous electrolytes.

Received 10th July 2026
Accepted 2nd October 2026

DOI: 10.1039/d6ta05828k

rsc.li/materials-a

1 Introduction

Solid-state electrolytes (SSEs) are promising replacements for flammable liquid electrolytes currently used in commercial Li-ion batteries, owing to their superior safety profiles and potential to enable high-energy-density lithium-metal anodes.^{1–3} However, developing an ideal solid-state ionic conductor remains a formidable challenge; such materials must simultaneously possess high ionic conductivity ($\sigma_{\text{Li}} > 10^{-3} \text{ S cm}^{-1}$), negligible electronic conductivity ($\sigma_e < 10^{-10} \text{ S cm}^{-1}$), a wide electrochemical stability window, and excellent mechanical and processing compatibility.^{4,5} Because no single material class fully meets these stringent criteria, extensive research has focused on a wide variety of structural

frameworks, including garnet, LISICON, sulfide, and perovskite structures.^{3,6–9}

Among these candidates, lithium-based antiperovskites (LiAPs) have attracted significant attention. LiAPs are electronically insulating and exhibit highly tunable ionic conductivities (10^{-6} to $10^{-3} \text{ S cm}^{-1}$) that are sensitive to proton substitution, halide composition, and processing history.^{10–14} Furthermore, they demonstrate excellent chemical and electrochemical stability against both solid and molten lithium metal.^{15,16} While pristine Li_3OCl exhibits outstanding room-temperature ionic conductivity ($>1 \text{ mS cm}^{-1}$), its highly hygroscopic nature routinely complicates phase-pure synthesis, frequently yielding protonated phases such as Li_2OHCl under realistic experimental conditions.^{15,17–19} Consequently, hydroxy-halide antiperovskites (Li_2OHX , where $\text{X} = \text{Cl, Br, I}$) have emerged as an independent class of promising SSEs. These materials possess exceptional thermodynamic stability, utilize earth-abundant elements, and feature low melting points (523–573 K) that

Department of Chemistry, Indian Institute of Technology Gandhinagar, Gujarat, 382355, India. E-mail: ram.sewak@iitgn.ac.in; amondal@iitgn.ac.in

ensure high wettability against oxide and metal electrodes, thereby minimizing interfacial resistance.^{20,21} Nevertheless, crystalline Li_2OHCl undergoes an unfavorable structural phase transition at ~ 345 K from a poorly conducting low-temperature orthorhombic phase ($\sim 1 \times 10^{-7} \text{ S cm}^{-1}$) to a highly conducting high-temperature cubic phase.^{22,23} While compositional engineering—such as halogen substitution in $\text{Li}_2\text{OHCl}_{1-x}\text{Br}_x$ or $\text{Li}_2(\text{OH})_{1-x}\text{Br}_x\text{Cl}$ —has successfully stabilized the room-temperature cubic phase and enhanced bulk conductivity to over $10^{-4} \text{ S cm}^{-1}$,^{14,24,25} the overall transport performance of these crystalline systems remains bottlenecked by severe grain-boundary resistance.^{26–28}

Amorphization represents a compelling strategy to eliminate these grain boundaries while preserving the favorable intrinsic properties of the antiperovskite framework. Amorphous or glassy solid electrolytes are homogeneous, isotropic, and lack internal phase boundaries.²⁹ Unlike their crystalline counterparts, in which discrete point defects mediate ion transport, glassy networks possess significant structural free volume, abundant low-energy librational vibrations, and a disordered potential-energy landscape that eliminates grain-boundary bottlenecks and promotes isotropic ion migration at lower activation energies, as demonstrated in both oxide and silicate glassy systems.^{30,31} Glassy frameworks have also been shown to effectively suppress lithium dendrite growth and enhance rate capabilities,^{32,33} as demonstrated in conventional lithium thiophosphate (LPS) and lithium phosphorus oxynitride (LiPON) glasses,^{34–38} as well as other superionic amorphous systems.^{39–43}

Importantly, first-principles simulations on sodium analogs ($\text{Na}_{3-x}\text{OH}_x\text{Cl}$) predict that glassy phases can exhibit remarkable ionic conductivities ($\sim 16 \text{ mS cm}^{-1}$ at 300 K), partially driven by an OH^- -mediated “paddlewheel” or gating mechanism.⁴⁴ In hydroxyl-containing antiperovskites, although the proton remains tightly bound to oxygen and does not contribute to net charge transport,⁴⁵ the rotational freedom of the OH^- groups can dynamically lower the activation barriers for adjacent mobile cations.^{46–49} This behavior aligns with the broader framework of phonon-assisted transport, where lattice dynamics and strongly anharmonic soft phonon modes dynamically lower activation barriers to facilitate cooperative ion hops across both crystalline and amorphous perovskite/antiperovskite superionic conductors.^{30,50–53} However, a detailed atomic-scale understanding of this rotational-translational coupling remains elusive, particularly within disordered or glassy phases where the distribution of local coordination environments is highly heterogeneous. While models suggest that paddlewheel mechanisms can persist even at low temperatures in glasses with limited network connectivity,⁵⁴ directly tracking the temporal and energetic correlations between OH^- reorientation and individual Li^+ hopping events requires spatial and temporal scales that are inaccessible to conventional *ab initio* molecular dynamics (AIMD) simulations.

To address these limitations, this work employs machine-learning interatomic potentials (MLIPs) trained on density functional theory (DFT) reference data. This approach enables highly accurate, long-timescale molecular dynamics (MD) simulations that realistically model the melt-quench synthesis

of glassy phases and capture rare ion-hopping events across metastable local environments.⁵⁵ We focus on the mixed-halide antiperovskite glass $\text{Li}_2\text{OHBr}_{0.5}\text{Cl}_{0.5}$, where compositional disorder breaks local symmetry, introducing a highly adaptive, heterogeneous potential energy landscape that maximizes configurational complexity near 500 K. Our simulations reveal that Li^+ transport in this glass proceeds *via* thermally activated hops through a dense network of distortion-induced metastable sites, aided by compositional lattice softening. Through meticulous event-based, autocorrelation, and conditional ensemble analyses, we isolate the exact relationship between local OH^- rotational dynamics and Li^+ transport. Our results show that while enhanced OH^- relaxation is temporally coupled to Li^+ hops both immediately before and after a transition, the large energy barriers and low frequencies associated with large-angle OH^- rotations rule out a perfectly synchronized, traditional paddlewheel model. Instead, we establish a revised mechanism wherein moderate, continuous OH^- reorientations transiently modulate the local migration landscape, providing a dynamically cooperative pathway for superionic conduction in disordered antiperovskite solid electrolytes.

2 Methods

2.1 Machine-learning potential development

To construct a robust MLIP for the $\text{Li}_2\text{OHBr}_{0.5}\text{Cl}_{0.5}$ mixed-halide system, initial atomic configurations were derived from the cubic $Pm\bar{3}m$ parent reported phase.⁵⁶ The pymatgen software package⁵⁷ was utilized to substitute 50% of the Cl sites with Br atoms. To identify the most stable ground-state configuration, all unique halide arrangements were evaluated *via* the Ewald summation method, and the structure minimizing the total electrostatic energy was selected. The resulting 40-atom supercell (16Li, 8O, 8H, 4Cl, and 4Br atoms) was fully relaxed using density functional theory as implemented in the Vienna *ab initio* Simulation Package (VASP).^{58,59} All DFT calculations utilized the projector augmented-wave (PAW) method to describe electron-ion interactions⁶⁰ and the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) for electron exchange–correlation.⁶¹ A plane-wave kinetic energy cutoff of 520 eV was applied, and long-range dispersion interactions were accounted for *via* the Grimme DFT-D3 correction scheme.⁶² Brillouin zone integration was performed using a Γ -centered k -point mesh with a reciprocal-space spacing of $0.3 \text{ \AA}^{-1}$. The electronic self-consistent field (SCF) loop was considered converged when the total energy difference between successive iterations fell below 10^{-6} eV .

To introduce configurational diversity into the initial training database, the optimized supercell was subjected to isotropic lattice scaling factors of 0.97, 1.00, and 1.03. For each volume condition, random atomic displacements of $0.03 \text{ \AA}$ were introduced to break structural symmetry, generating 50 distinct perturbed structures per scaling factor (150 configurations in total). Short *ab initio* molecular dynamics simulations were then performed for each configuration at 300 K in the NVE (micro-canonical) ensemble for 100 fs, with a time step of 0.5 fs. The equations of motion were integrated using the velocity Verlet

algorithm.⁶³ Atomic coordinates, energies, and forces were extracted from 40 randomly sampled time steps along each trajectory to form the seed dataset.

Using this dataset, a deep neural network (DNN) potential was developed *via* 15 concurrent-learning iterations within the DP-GEN active-learning framework.⁶⁴ This iterative scheme systematically samples the potential energy surface across a wide thermodynamic range, capturing both crystalline environments and the amorphous configurations relevant to the glassy state. During the active-learning cycle, four independent models were initialized with identical neural network architectures and different random seeds to account for stochastic optimization behavior. The deep potential models were trained using the DeePMD-kit package.^{65,66} Local atomic environments were mapped *via* the `se_e2_a` descriptor,⁶⁷ which encodes many-body radial and angular geometric information from interatomic distances while strictly preserving permutation, translation, and rotation symmetries. The embedding network utilized a ResNet-like architecture^{68,69} with hidden layer dimensions of (25, 50, 100), passing continuous latent descriptors to a fitting network composed of three layers with 240 nodes each. The parameters were optimized over 6×10^5 iterations by minimizing the loss function:

$$L = p_e \Delta E^2 + \frac{p_f}{3N} \sum_i \Delta F_i^2$$

where N is the number of atoms, and ΔE^2 and ΔF_i^2 denote the squared errors of the total energy and the component-wise atomic forces, respectively. The prefactors p_e and p_f dynamically regulated the loss contributions; p_e was gradually increased from 0.2 to 8, while p_f was decreased from 1000 to 1 to prioritize force accuracy in early training stages and energy consistency during late-stage refinement. The learning rate was exponentially decayed from 1×10^{-3} to 3.51×10^{-8} .

Exploration steps within the DP-GEN cycle were executed through deep potential molecular dynamics (DPMD) simulations using LAMMPS⁷⁰ interfaced with DeePMD-kit. Exploration trajectories were extended up to 800 K to explicitly sample disordered structures and high-temperature ionic transport pathways. For each production run, trajectories were driven by a single candidate model, while forces were concurrently predicted by all four ensemble models. Model consistency was evaluated by monitoring the maximum standard deviation of the atomic forces:

$$\zeta = \max_i \sqrt{\langle |\mathbf{F}_i - \bar{\mathbf{F}}_i|^2 \rangle}$$

where $\mathbf{F}_i$ is the force vector predicted for atom i by model i , and $\bar{\mathbf{F}}_i$ is the corresponding four-model average. Configurations yielding force deviations $\zeta > 1.0 \text{ eV } \text{\AA}^{-1}$ were flagged as under-sampled regions of configuration space. These structures were automatically extracted, subjected to single-point DFT calculations using the reference VASP settings, and appended to the training database. This active-learning cycle was repeated until the fraction of high-deviation configurations fell below 0.01% of the total explored space, ensuring comprehensive coverage and high fidelity of the final potential energy surface.

2.2 Glass phase preparation and transport simulations

To generate the glassy phase from the crystalline state, large-scale MD simulations were executed using the fully converged DNN potential. A $3 \times 3 \times 3$ supercell was constructed from the equilibrated unit cell, yielding a cubic simulation box with a lattice parameter of 23.46 Å and containing 1080 atoms. This system size was selected to minimize periodic finite-size effects and ensure statistically meaningful sampling of long-range ion migration pathways. The crystalline supercell was gradually heated from 300 K to a peak annealing temperature of 750 K and equilibrated for 5 ns within the isothermal-isobaric (NpT) ensemble. This elevated annealing temperature was chosen to induce complete structural disorder and accelerate amorphization, effectively bypassing the long kinetic timescales associated with experimental glass formation within computationally accessible MD limits. To confirm that the framework retained its structural integrity as a highly disordered amorphous solid rather than undergoing unphysical vapor degradation or phase separation, the resulting networks were systematically audited for thermodynamic stability and short-to medium-range atomic connectivity.

Prior to collecting transport statistics, the disordered configurations were quenched and equilibrated under NpT conditions at target temperatures of 450, 500, 600, and 700 K. This step allowed the simulation cell volume to fully relax and eliminate residual macro-stresses intrinsic to the melt-quench process. Following this structural relaxation, long-timescale production runs were performed in the canonical (NVT) ensemble for up to 4 ns to capture the full spectrum of Li^+ -ion dynamical behavior. Proper equilibration across all production windows was verified by continuously monitoring the convergence of temperature, pressure, cell volume, and total potential energy. The combined simulation timescales and system dimensions provide highly converged statistical sampling, ensuring the accurate determination of ionic conductivities, diffusion coefficients, and transport activation energies within the glassy framework.

3 Results and discussion

3.1 Validation of the deep neural network potential

To ensure that the DNN-based MLIP accurately captures non-equilibrium transition states—such as transient Li^+ hopping bottlenecks and large-angle OH^- polyanionic reorientations—the training set was systematically refined through successive DP-GEN active-learning iterations up to 800 K. During this iterative workflow, configurations exhibiting high force uncertainties (ζ) were adaptively identified and incorporated into the training database, progressively eliminating poorly represented high-energy, amorphous, and dynamically distorted regions of the potential energy surface. The training curves for the final ensemble models (Fig. S1) display a smooth, monotonic decay in both energy and force losses, demonstrating stable convergence without overfitting. After approximately 6×10^5 optimization steps, the DNN model achieved internal fitting errors of $\sim 7.57 \times 10^{-1} \text{ eV}$ for total energies and $\sim 2.44 \times 10^{-3} \text{ eV } \text{\AA}^{-1}$ for

atomic forces. These values align with the high-fidelity accuracy benchmarks reported for DPMD simulations of multi-component, disordered solid-state systems,^{55,71,72} confirming the potential's capacity to reproduce DFT-level forces critical for capturing long-range ion transport. To rigorously evaluate the predictive capability of the trained DNN potential, we directly compared its energy and force predictions against explicit DFT reference calculations using an independent test set not included during model training (Fig. 1). The model demonstrated exceptional generalization, yielding an energy root-mean-square error (RMSE) of 6.42×10^{-4} eV per atom and a force RMSE of 2.31×10^{-2} eV Å⁻¹. The narrow error distributions and tight linear correlation between the DFT reference values and DNN predictions confirm that the model accurately captures both subtle thermodynamic trends and intricate local force variations across complex, phase-transformed landscapes. This level of accuracy is highly critical for glassy antiperovskites, where structural distortions and fluctuating local coordination environments strongly dictate the underlying lithium-ion migration pathways.

To further evaluate the accuracy of the machine-learning potential in capturing local potential-energy-surface curvature, the phonon density of states (DOS) derived from MLMD was benchmarked directly against DFT calculations derived phonon DOS (Fig. S2). The element-projected phonon DOS shows excellent agreement across all atomic species (Li, O, H, Cl, and Br). The MLIP accurately reproduces the low-frequency acoustic and optic halide modes, the broad intermediate-frequency region corresponding to Li-O cage vibrations, and the high-frequency O-H stretching band. This close correspondence between the vibrational spectrum and the phonon density distribution confirms that the neural network potential reliably models the local force-constant landscape, soft-mode lattice dynamics, and vibrational coupling that facilitate Li⁺ transport.

3.2 Structural amorphization and ionic transport dynamics

The structural and thermodynamic characteristics of the glassy Li₂OHCl_{0.5}Br_{0.5} matrix were systematically evaluated following melt-quench NpT molecular dynamics protocols. Thermodynamically, glass formation is accompanied by a modest volumetric expansion relative to the 300 K crystalline reference cell (13 798.96 Å³). The equilibrated glass volume evolves from 14 002.32 Å³ at 450 K to 14 734.63 Å³ at 700 K, corresponding to relative volume changes of 1.47% (450 K), 2.58% (500 K), 4.02% (600 K), and 6.78% (700 K). This mild volume expansion reflects the creation of additional free volume and lower structural density characteristic of amorphized networks, consistent with melt-quench studies on related antiperovskite glass formers.⁴⁴

The structural transition from the crystalline to the glassy state upon cooling from 750 K was further verified through simulated X-ray diffraction (XRD) and radial distribution function (RDF) analyses. Compared to the parent crystalline phase, the calculated XRD patterns of the glassy phase show a complete disappearance of sharp Bragg reflections at higher angles (Fig. S3), signaling a loss of long-range translational order. A similar suppression of high-angle diffraction peaks has been observed during the experimental synthesis of Li₂OHCl_{0.5}Br_{0.5} glass and was attributed to structural amorphization.⁷³ The broad low-angle intensity maxima in the calculated diffraction profile arise from diffuse scattering associated with short-range polyhedral correlations within the amorphous network, rather than residual long-range order or finite-size effects from the 1080-atom supercell. This reciprocal-space signature-characterized by lost high-angle periodicity and retained short-range diffuse intensity-matches experimental diffraction profiles reported for amorphized antiperovskite electrolytes,⁷³ as well as the real-space RDF analysis.

Additionally, the computed RDFs comparing the crystalline and amorphous phases reveal pronounced peak broadening across the atomic pairs (Fig. S4), further confirming the

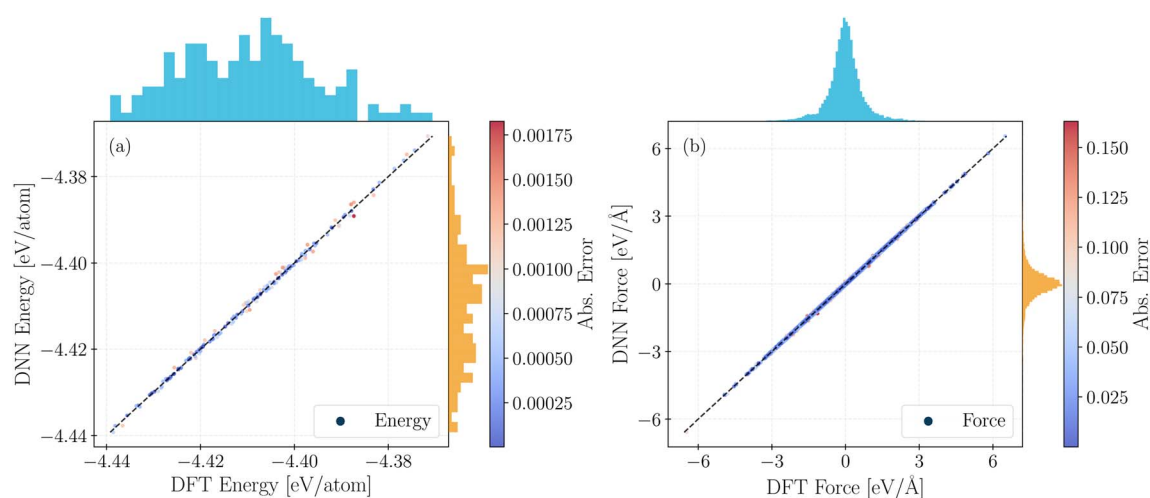


Fig. 1 Evaluation of the trained deep neural network potential against independent DFT test data. Parity plots comparing DFT reference values and DNN predictions for (a) total energies and (b) atomic forces, where the dashed lines denote ideal linear correlation. Marginal histograms display the data density distributions, and the color coding represents the absolute prediction errors, demonstrating excellent model generalization across diverse configurations.

emergence of a highly disordered framework. In particular, the Li–Li and Li–O RDFs in the crystalline phase exhibit sharp, well-defined peaks extending across multiple coordination shells, characteristic of long-range periodic order. Upon amorphization, short-range coordination is preserved, but the first-neighbor peaks undergo pronounced broadening, reflecting a broad distribution of local Li–O bond lengths and Li–Li separations driven by mixed-halide disorder and structural distortions. Beyond the second coordination sphere, long-range structural oscillations are strongly damped in the glass phase, indicating the loss of long-range translational symmetry. This combination of preserved short-range polyhedral connectivity and diminished long-range structural correlations is consistent with the broad features observed in the XRD patterns, confirming the structurally disordered, energy-heterogeneous nature of the amorphous network.⁷⁴

To evaluate long-range ionic transport within this disordered network, mean-squared displacement (MSD) analysis was performed on MD trajectories across the investigated temperature range. The time-dependent MSD for a given atomic species i is defined as:

$$\text{MSD}_i(t) = \left\langle \frac{1}{N_i} \sum_{c=1}^{N_i} \left| \mathbf{r}_i^c(t + t_0) - \mathbf{r}_i^c(t_0) \right|^2 \right\rangle \quad (1)$$

where N_i represents the total number of atoms of species i , $\mathbf{r}_i^c(t)$ is the position vector of atom c at time t , and $\langle \dots \rangle$ denotes averaging over multiple overlapping time origins (t_0). The MSD and corresponding diffusion coefficients (D) were evaluated from the linear regime using the Einstein relation. To improve statistical convergence and minimize sampling noise, the MSDs were computed using the windowed time-averaging method implemented in the MDAnalysis package,⁷⁵ thereby averaging over multiple time origins (t_0) across the long-timescale production trajectories for each time lag (τ). This origin-averaging protocol provides rigorous statistical sampling of individual hopping events, ensuring that the resulting self-diffusion coefficients and Nernst–Einstein ionic conductivities are free from single-origin statistical artifacts.

As illustrated in Fig. 2a, the semilogarithmic plot of the Li^+ -ion MSD exhibits two distinct transport regimes. At very short timescales ($t < 1$ ps), the MSD displays a quadratic time dependence ($\propto t^2$), which is characteristic of the ballistic regime dominated by localized inertial vibrations. At longer times, the MSD transitions into a strictly linear regime ($\propto t$), signaling the onset of continuous, long-range diffusive transport and confirming that lithium ions serve as the primary mobile charge carriers in glassy $\text{Li}_2\text{OHCl}_{0.5}\text{Br}_{0.5}$.

To verify the statistical reproducibility of the simulated glassy matrix, two additional independent glass models (Model 2 and Model 3) were generated *via* separate melt-quench trajectories and subjected to identical equilibration and sampling protocols. The transport and topological metrics showed excellent consistency across all independent realizations. At 600 K, the ionic conductivities of the three models varied by less than 10%, yielding values of $2.47 \times 10^{-1} \text{ S cm}^{-1}$ (Model 1 as initial configuration), $2.68 \times 10^{-1} \text{ S cm}^{-1}$ (Model 2), and $2.45 \times 10^{-1} \text{ S cm}^{-1}$ (Model 3). Furthermore, site-distribution analysis confirmed matching structural disorder, with average activation energies spanning a narrow range of 0.292 to 0.299 eV (Table S1 and Fig. S5). This quantitative agreement confirms that the reported ion transport and dynamic mechanisms reflect intrinsic thermodynamic properties of the amorphous network rather than configuration-specific sampling artifacts.

Impedance spectroscopy studies on hydroxyl-containing antiperovskites have occasionally suggested that measured ionic conductivities might include contributions from vehicular or cooperative proton transport.²⁴ To evaluate this possibility, the proton MSD was systematically monitored (Fig. S6). In contrast to the lithium behavior, the proton MSD reaches a strict plateau before the end of the simulation window. Crucially, the maximum proton displacement is bounded at $\sim 2 \text{ \AA}^2$, which is substantially shorter than the average O–O distance of $3.77 \text{ \AA}$ in the glass matrix. This highly localized spatial confinement explicitly rules out long-range proton migration, confirming that a proton-mediated Grotthuss mechanism^{76,77} is

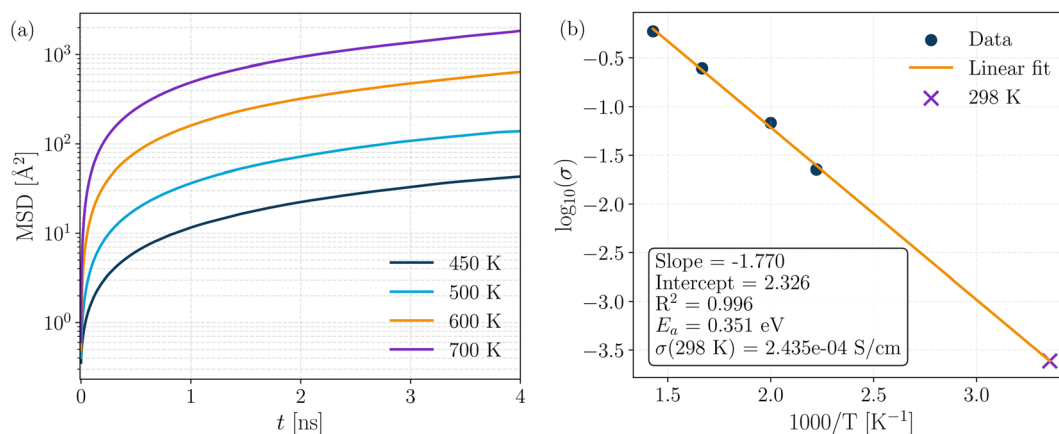


Fig. 2 (a) Semilogarithmic plot of the temperature-dependent mean square displacement (MSD) of Li^+ ions in glassy $\text{Li}_2\text{OHCl}_{0.5}\text{Br}_{0.5}$, highlighting the transition from short-time ballistic motion to long-time linear diffusion. (b) Arrhenius plot of the extracted Li^+ ionic conductivity, including the calculated activation energy (E_a) and the extrapolated room-temperature value at 300 K.

not operative in glassy $\text{Li}_2\text{OHCl}_{0.5}\text{Br}_{0.5}$ and that net ionic conductivity is purely cationic.

Following the identification of the long-time diffusive regime, the self-diffusion coefficients (D_{Li}) of the lithium ions were computed using the Einstein relation:

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \text{MSD}(t) \quad (2)$$

The extracted diffusion coefficients were subsequently converted into tracer ionic conductivities (σ) *via* the Nernst-Einstein relation:

$$\sigma = \frac{e^2}{Vk_{\text{B}}T} z_{\text{Li}}^2 N_{\text{Li}} D_{\text{Li}} \quad (3)$$

where e is the elementary charge, V is the equilibrium system volume, k_{B} is the Boltzmann constant, T is the absolute temperature, and z_{Li} and N_{Li} denote the valency (+1) and total number of lithium ions in the simulation cell, respectively. The temperature dependence of the calculated conductivity was evaluated *via* Arrhenius analysis (Fig. 2b) to determine the bulk migration activation energy (E_{a}) and to extrapolate the transport performance to ambient conditions. At 298 K, the extrapolated ionic conductivity of the glassy $\text{Li}_2\text{OHCl}_{0.5}\text{Br}_{0.5}$ phase reaches $2.43 \times 10^{-4} \text{ S cm}^{-1}$ with a remarkably low activation energy of 0.35 eV. To independently validate the room-temperature conductivity obtained *via* Arrhenius extrapolation from high-temperature MD simulations (450–700 K), an additional direct DPMD simulation was performed at 298 K. The direct 298 K simulation yielded an ionic conductivity of $3.99 \times 10^{-4} \text{ S cm}^{-1}$, showing good agreement with the extrapolated value of $2.43 \times 10^{-4} \text{ S cm}^{-1}$. The consistency between direct simulation and linear Arrhenius extrapolation confirms that the structural relaxation and coupled Li^+ transport mechanisms remain kinetically active and mechanistic trajectory changes do not occur across the ambient-to-elevated temperature domain.

The calculated room-temperature ionic conductivity of glassy $\text{Li}_2\text{OHCl}_{0.5}\text{Br}_{0.5}$ was evaluated alongside benchmark experimentally reported glassy lithium-ion electrolytes. Amorphous Li_2S - SiS_2 -based electrolytes exhibit room-temperature conductivities of $6.9 \times 10^{-4} \text{ S cm}^{-1}$,⁷⁸ while highly conducting $80\text{Li}_2\text{S}$ $20\text{P}_2\text{S}_5$ glass reaches $8.8 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature.⁷⁹ More broadly, representative sulfide glass electrolytes span conductivities from approximately 10^{-5} to $10^{-3} \text{ S cm}^{-1}$, depending on chemical composition and processing conditions.⁸⁰ In addition, a glassy ZIF-4-based quasi-solid electrolyte has been reported to exhibit a conductivity of $1.61 \times 10^{-4} \text{ S cm}^{-1}$ at 30 °C.⁸¹ The conductivity predicted in this work therefore falls squarely within the experimentally demonstrated range for fast-ion conducting glassy Li^+ solid electrolytes. Direct quantitative comparisons should nevertheless be made with caution due to variations in chemical composition, Li^+ carrier concentration, processing history, measurement temperature, and the distinction between tracer conductivity derived from molecular dynamics simulations and experimentally measured macroscopic ionic conductivity.

To contextualize these transport properties, Table 1 compares our glassy-phase benchmarks with previously reported experimental values for crystalline analog systems. This comparison underscores that amorphization yields a massive improvement over the crystalline counterpart, accelerating room-temperature ionic transport by over two orders of magnitude. The simultaneous drop in the migration barrier from 0.61 eV to 0.35 eV indicates that the structurally disordered network fundamentally alters the potential energy landscape, offering highly favorable, continuous percolation pathways that bypass the severe steric or electrostatic bottlenecks typical of the crystalline lattice.

3.3 Structural heterogeneity and spatial distribution of cations

To elucidate the microscopic origin of the enhanced Li^+ mobility in the glassy state, we analyzed the spatial distribution of the lithium ions and their temperature-dependent evolution. In amorphous solids, structural disorder and localized lattice distortions break the symmetry of the potential energy surface, generating a highly heterogeneous energy landscape. This enables Li^+ ions to occupy not only deep basins corresponding to standard crystallographic positions but also shallow, distortion-induced metastable environments. To characterize these dynamically accessible environments, we utilized the time-averaged occupancy grid (TAOG) method—a volumetric density-based approach. The simulation cell was discretized into a fine three-dimensional mesh of volumetric elements (voxels), and the instantaneous positions of all mobile Li^+ ions were mapped onto this grid at every production time step. Accumulating these voxel occupancies over the entire trajectory yields a 3D spatial probability density distribution that represents the local residence probability of the cations. Regions of high occupancy were mapped against the nominal parent crystallographic Wyckoff positions to identify parent-topology-associated environments sites, while additional high-density spatial nodes emerging from the glassy-phase distortions were classified as metastable interstitial sites. Within these distortion-induced locations, Li^+ ions remain localized for a significant fraction (~95%) of the typical residence lifetime observed at stable nodes (Fig. S7). Importantly, the total number of identified sites does not match the stoichiometric count of Li^+ ions in the simulation box; rather, these topological sites represent the total ensemble of discrete potential energy minima mapped out by the long-range trajectories over time.

As summarized in Table 2, both the number of metastable interstitial environments and the aggregate number of spatial nodes maximize distinctly at 500 K. This trend indicates that the number of dynamically accessible, local coordination environments peaks in this temperature regime, reflecting a maximization of the configurational heterogeneity intrinsic to the glassy state. Upon further heating beyond 500 K, the population of metastable sites systematically contracts, accompanied by a minor expansion of stable Wyckoff-like nodes. This behavior represents a thermally activated structural relaxation in which the highly strained amorphous framework undergoes local

Table 1 Comparison of extrapolated room-temperature ionic conductivity ($\sigma_{298\text{ K}}$) and transport activation energy (E_a) of glassy $\text{Li}_2\text{OHCl}_{0.5}\text{Br}_{0.5}$ with experimentally reported crystalline lithium hydroxy-halide antiperovskites measured via electrochemical impedance spectroscopy (EIS)

Material system	Phase morphology	$\sigma_{298\text{ K}}$ [S cm^{-1}]	E_a [eV]	References
$\text{Li}_2\text{OHCl}_{0.5}\text{Br}_{0.5}$	Glassy	2.43×10^{-4}	0.35	This work
$\text{Li}_2\text{OHCl}_{0.5}\text{Br}_{0.5}$	Crystalline	1.54×10^{-6}	0.61	25
$\text{Li}_2\text{OHCl}_{0.9}\text{Br}_{0.1}$	Crystalline	2.52×10^{-6}	0.52	25
Li_2OHCl	Crystalline	1.93×10^{-6}	0.53	25

Table 2 Temperature-dependent distribution of Li^+ -ion sites identified via TAOG analysis, categorized into parent-topology-associated environments and distortion-induced metastable interstitial environments

T [K]	Total extracted sites	Parent-topology-associated sites	Metastable sites
450	452	218	234
500	485	237	248
600	463	243	220
700	442	249	193

reorganization toward lower-energy environments. This structural evolution corresponds closely with the experimental differential scanning calorimetry (DSC) profiles reported by Milan *et al.*⁷³ for $\text{Li}_2\text{OHCl}_{0.5}\text{Br}_{0.5}$. In their work, an endothermic slope associated with the glass transition was followed immediately by distinct exothermic features near 530 K, attributed to structural rearrangements and sub-nanometer partial crystallization. Their findings also noted that a residual crystalline characteristics frequently persists in experimental samples even under optimized synthesis conditions, echoing the coexistence of stable Wyckoff networks and highly disordered glassy pathways observed in our transport models.

It is important to clarify that the present atomistic model represents a homogeneous amorphous matrix and does not explicitly reproduce the mesoscale crystalline-amorphous microstructures or phase coexistence that may occur in experimental samples. The concurrent presence of parent-like coordination nodes and distortion-induced metastable Li^+ environments identified by TAOG within the periodic DPMD cell reflects local topological heterogeneity within the glass network, rather than literal domain-separated crystalline and amorphous phases. Consequently, the calculated ionic conductivities and migration mechanisms reported here represent the intrinsic transport properties of the purely glassy phase. The effective macroscopic conductivity of an experimental specimen – which may contain residual crystalline grains – will additionally depend on phase volume fractions, grain boundary impedance, and mesoscale percolative connectivity.

To ensure that the 1080-atom simulation cell ($3 \times 3 \times 3$ supercell, containing 432 Li^+ ions) adequately captures the structural heterogeneity and Li^+ transport pathways of the amorphous electrolyte, system-size convergence tests were conducted using a larger $4 \times 4 \times 4$ supercell containing 2560 atoms (1024 Li^+ ions) by evaluating Li^+ ions MSD (Fig. S8). The

calculated Li^+ conductivity decreases from $6.80 \times 10^{-2} \text{ S cm}^{-1}$ for the 1080-atom cell to $6.71 \times 10^{-2} \text{ S cm}^{-1}$ for the 2560-atom cell, corresponding to a very small variation of $\sim 1.32\%$. This close agreement indicates that the 1080-atom cell provides sufficient statistical sampling of the local disordered environments and ion-transport pathways, while the overall transport kinetics and conductivity are not significantly influenced by finite-size effects or periodic supercell artifacts. Nevertheless, as with any atomistic simulation of a structurally amorphized material, finite cell dimensions and accessible simulation timescales necessarily sample only a representative subset of the extremely broad configurational ensemble characteristic of a macroscopic glass. Therefore, the TAOG-derived spatial nodes should be interpreted as representative, dynamically accessible metastable environments sampled along the simulated trajectory, rather than as an exhaustive catalog of all possible potential-energy minima in a macroscopic amorphous matrix. Within these practical sampling limits, the resulting spatial mapping provides a realistic microscopic framework for describing the heterogeneous energy landscape and the dynamically accessible transport environments encountered by Li^+ ions.

Taken together, the topological metrics capturing the heterogeneous energy landscape, along with the reciprocal- and real-space structural analyses, consistently demonstrate the amorphous nature of the simulated matrix. The strong suppression of high-angle Bragg reflections in the XRD pattern, together with broadened first-neighbor peaks and rapidly damped correlations in the RDFs, indicates the loss of long- and intermediate-range translational order while retaining chemically bonded short-range structural correlations. This structural disorder is further reflected in the coexistence of distortion-induced metastable Li^+ sites with sites associated with the parent-crystalline topology, providing direct evidence for the breakdown of a uniform crystal lattice.

3.4 Local vibrational dynamics and anisotropic coordination environments

At the atomistic level, Li^+ ions primarily undergo localized vibrational motion within potential wells formed by neighboring framework anions, only occasionally acquiring sufficient thermal energy to hop between adjacent coordination sites. This behavior is clearly visible in the distributions of Li^+ -ion vibrational amplitudes around their occupation sites (Fig. S9). The vibrational amplitude is defined as the directional half-stroke accumulated over consecutive frame-to-frame displacements until a velocity reversal, providing a reference-free

measure of intra-cage thermal excursions without relying on fixed initial or time-averaged spatial coordinates. The non-zero maximum near ~ 0.4 Å reflects the characteristic magnitude of most frequently sampled vibrational turnarounds within local polyhedral cages.

At lower temperatures (450 and 500 K), Gaussian fitting of the localized atomic displacements yields a tight $\pm 2\sigma$ range of 1.10–1.38 Å, indicating that the cations remain vibrationally confined within their local cages for approximately 95% of the simulation time. At elevated temperatures (600 and 700 K), this displacement distribution extends up to ~ 2 Å, capturing strongly anharmonic excursions. Thus, the systematic shift toward larger amplitudes with temperature indicates softening of the local trapping environments, while true inter-site hopping distances and kinetics are determined independently from discrete trajectory tracking between TAOG-derived sites.

To quantify the clock rate of these localized oscillations, vibrational frequency spectra were extracted for the caged lithium ions (Fig. 3). The profiles yield average attempt frequencies (ν_{attempt}) ranging between 3.22×10^{12} and $3.43 \times 10^{12} \text{ s}^{-1}$ across the investigated temperature range, demonstrating that the intrinsic vibrational timescale is only weakly temperature-dependent. These values show excellent agreement with typical AIMD benchmarks (10^{12} – 10^{13} Hz) reported for related fast-ion conductors, validating the reliability of the DPMD framework.^{82–84} This characteristic frequency defines the prefactor for thermally activated macroscopic diffusion. In accordance with the Meyer–Neldel rule,⁸⁵ variations in these local attempt frequencies often scale with the migration barriers, as higher activation barriers entail a larger collective

displacement of the framework and a corresponding increase in vibrational entropy at the transition state.

Crucially, the distinct shoulder-like feature observed in the Li^+ vibrational spectra (Fig. 3) represents a physical consequence of the anisotropic coordination environment within the antiperovskite framework. In cubic lithium-rich antiperovskites (Li_3OX and Li_2OHX), each Li^+ ion occupies a face-sharing octahedral vertex coordinated by two axial oxygen/hydroxyl anions and four equatorial halide anions.⁸⁶ Because the Li–O bonds are significantly shorter and stiffer than the corresponding Li–halide bonds (e.g., nominal bond lengths of ~ 1.95 Å versus ~ 2.38 Å in crystalline Li_2OHCl), the restoring force constants experienced by a caged lithium ion are highly directional.⁴⁹ This severe mechanical anisotropy splits the vibrational density of states into distinct high- and low-frequency components, generating the characteristic split-band profile. Compositional engineering *via* Br^- substitution at the Cl^- sites further breaks this local symmetry. Owing to its larger ionic radius and more polarizable electron cloud, bromine softens the local lattice and weakens the Li–X ($\text{X} = \text{Cl}, \text{Br}$) interactions, systematically shifting the low-frequency vibrational modes downward. This mass and size effect is clearly reflected in the pure-halide reference systems, Li_2OHCl and Li_2OHBr (Fig. S10). Within the mixed-halide $\text{Li}_2\text{OHBr}_{0.5}\text{Cl}_{0.5}$ glass, the coexistence of both chlorine- and bromine-centered local environments broadens the distribution of these interatomic force constants, making the spectral shoulder more pronounced. As the temperature is raised, thermal expansion, macro-lattice softening, and enhanced OH^- orientational disorder combine to shift and broaden these low-frequency components. This

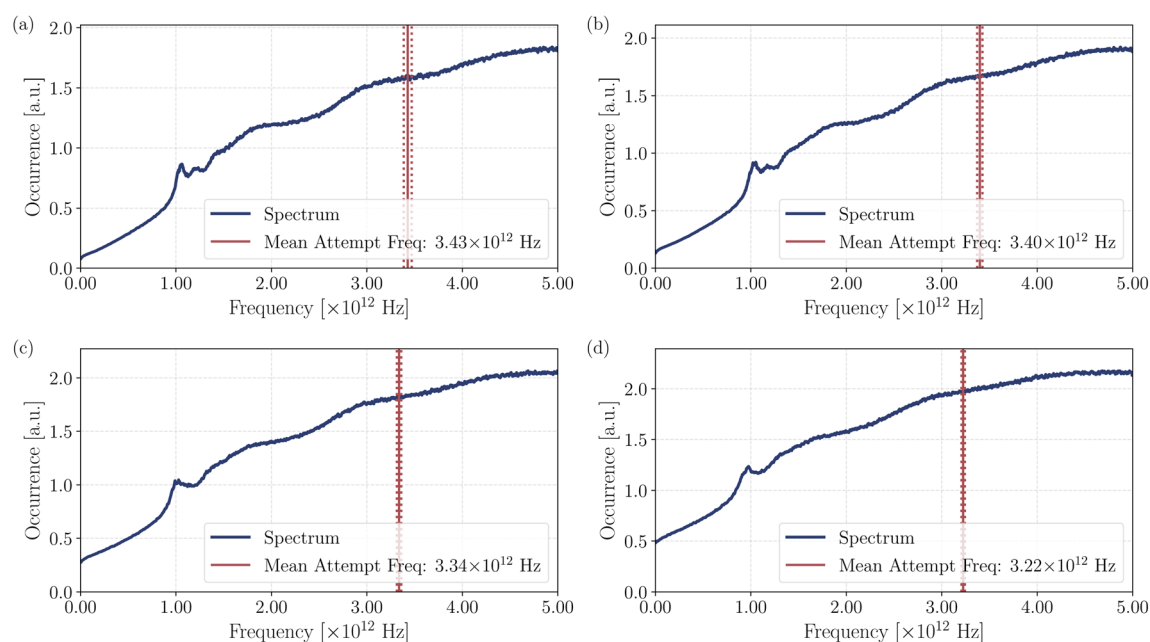


Fig. 3 Temperature-dependent vibrational frequency spectra of diffusing Li^+ ions in glassy $\text{Li}_2\text{OHCl}_{0.5}\text{Br}_{0.5}$ at (a) 450 K, (b) 500 K, (c) 600 K, and (d) 700 K. The solid vertical red lines indicate the mean vibrational attempt frequency (ν_{attempt}), while the dotted red lines mark one standard deviation, illustrating the consistent timescale of local cation oscillations. The characteristic low-frequency shoulder originates from the intrinsic bonding anisotropy between the stiff axial Li–O and softer equatorial Li–halide coordination shells.

thermal damping weakens the structural restoring forces confining the cations, effectively lowering the local migration barriers and enabling Li^+ ions to readily escape their coordination cages through dynamically widened halide bottlenecks.

To explore the microscopic transport mechanism of the amorphous state, we conducted an event-based jump analysis. Within this disordered framework, long-range diffusion arises from successive, localized hops between transient occupation sites rather than migration through a periodic lattice. These local minima are identified from the TAOG mapping, with a successive hop recorded when a Li^+ ion transitions between neighboring TAOG nodes. To separate genuine site-to-site jumps from local intra-cage rattling, each site was assigned a capture radius (R_{site}) equal to twice the mean Li^+ vibrational amplitude.⁸² To eliminate uncorrelated recrossing events, a successful hop required the ion to vacate the origin volume and maintain continuous residence within the target site radius for a minimum threshold of 100 trajectory frames (0.1 ps). Instantaneous forward-backward fluctuations that failed to satisfy this residence criterion were filtered out as local vibrational excursions, ensuring that the extracted jump kinetics reflect true transport-active diffusion events.

For each distinct conduction channel (i), defined as a specific spatial migration pathway connecting a unique pair of neighboring local minima identified *via* TAOG analysis, all successful Li^+ transitions between these sites are assigned to the corresponding channel. The parameter N_i denotes the number of unique Li^+ ions that undergo at least one successful transition through channel i during the analyzed trajectory, representing the effective carrier population associated with that pathway rather than the total Li^+ ion count of the cell. This channel-specific carrier population is subsequently used to normalize the hopping frequency and evaluate the corresponding activation barrier relative to the local attempt frequency prefactor (ν_{attempt}) determined in the preceding section. The mean jump rate for a specific migration channel i , defined as $J_i = N_{\text{events},i}/t$, was extracted from the total number of observed hops during the simulation time t , directly mapping microscopic hopping dynamics to macroscopic transport metrics. The operational activation energy ($E_{a,i}$) for each distinct hop type was estimated from its effective jump frequency using the relation:

$$E_{a,i} = -k_B T \ln \left(\frac{J_i}{N_i \nu_{\text{attempt}}} \right) \quad (4)$$

where k_B is the Boltzmann constant, T is the temperature. Unlike static computational methods such as the nudged elastic band (NEB) or bond-valence site energy techniques – this dynamic formalism inherently captures both the local energetic barriers and the configurational entropic contributions that govern fast-ion migration at realistic temperatures. Moreover, the spectral profiles yield characteristic local vibrational frequencies of caged Li^+ ions in the range of $3.22\text{--}3.43 \times 10^{12} \text{ s}^{-1}$, which characterize the intrinsic timescale of localized intra-cage Li^+ oscillations and are used as the attempt-frequency prefactor (ν_{attempt}) in the kinetic jump analysis. Consistent with recent insights into antiperovskite transport kinetics,⁸⁷ this

local frequency is not intended to represent a unique transport-active phonon mode or a global spectral mean of all lattice vibrations. Instead, actual diffusion kinetics and activation barriers are evaluated directly from explicit spatial hopping events (J_i) observed along the DPMD trajectories.

The distribution of the 20 highest-energy activation barriers associated with accessible hopping channels across different temperatures is presented in Fig. 4. As the temperature increases, the population of low-energy migration pathways expands substantially, driving down the overall ensemble-averaged activation energy (Fig. 4, inset). In stark contrast to crystalline solid electrolytes, which feature rigid, well-defined hopping topologies and relatively uniform migration barriers, the glassy phase introduces a structural continuum of metastable sites with heterogeneous connectivity, resulting in a characteristically broad distribution of activation energies. This rugged energy landscape is visibly manifested in the temporal evolution of individual Li^+ -ion displacements shown in Fig. 5 for the 20 most mobile cations. At lower temperatures, the displacement profiles are heavily dominated by extended plateaus, capturing severe structural confinement and localized rattling within local coordination cages. Intermittently, certain ions exhibit abrupt, discontinuous changes in position that correspond to successful hops between neighboring stable and metastable sites, before being trapped in a new vibrational cage. Such clear, step-like trajectories are the hallmark of a hopping-mediated diffusion mechanism in solid-state conductors. Elevating the temperature markedly shortens the residence time within these local cages, promoting more frequent and continuous hopping sequences that manifest as enhanced macroscopic mobility.

The present approach differs from the conventional Vineyard transition-state treatment⁸⁸ in that it does not require the identification of a specific saddle point or the calculation of the complete vibrational spectrum for each individual migration event. Instead, it characterizes the average attempt frequency from the collective vibrational motion of mobile ions within their local coordination environments. In this sense, the intra-cage vibrational motion of an ion is treated as a sequence of attempts to overcome the local migration barrier. This distinction is particularly important for disordered and glassy materials, where numerous non-equivalent migration pathways exist, and identifying individual saddle points using static potential-energy surface calculations is impractical. By extracting attempt frequencies directly from finite-temperature atomic trajectories, this approach naturally incorporates anharmonicity, thermal expansion, and temperature-dependent lattice softening, while providing direct insight into how local framework compliance influences ion mobility.

Beyond isolated events, individual Li^+ hops can transiently perturb the local electrostatic and structural fields, creating short-lived potential energy minima that may lower the barrier for neighboring ions, thereby triggering correlated or multi-ion collective migration. These multi-ion correlated hopping events were quantified by analyzing spatial and temporal correlations between pairs of discrete Li^+ jump events. A pair of hops (i, j)

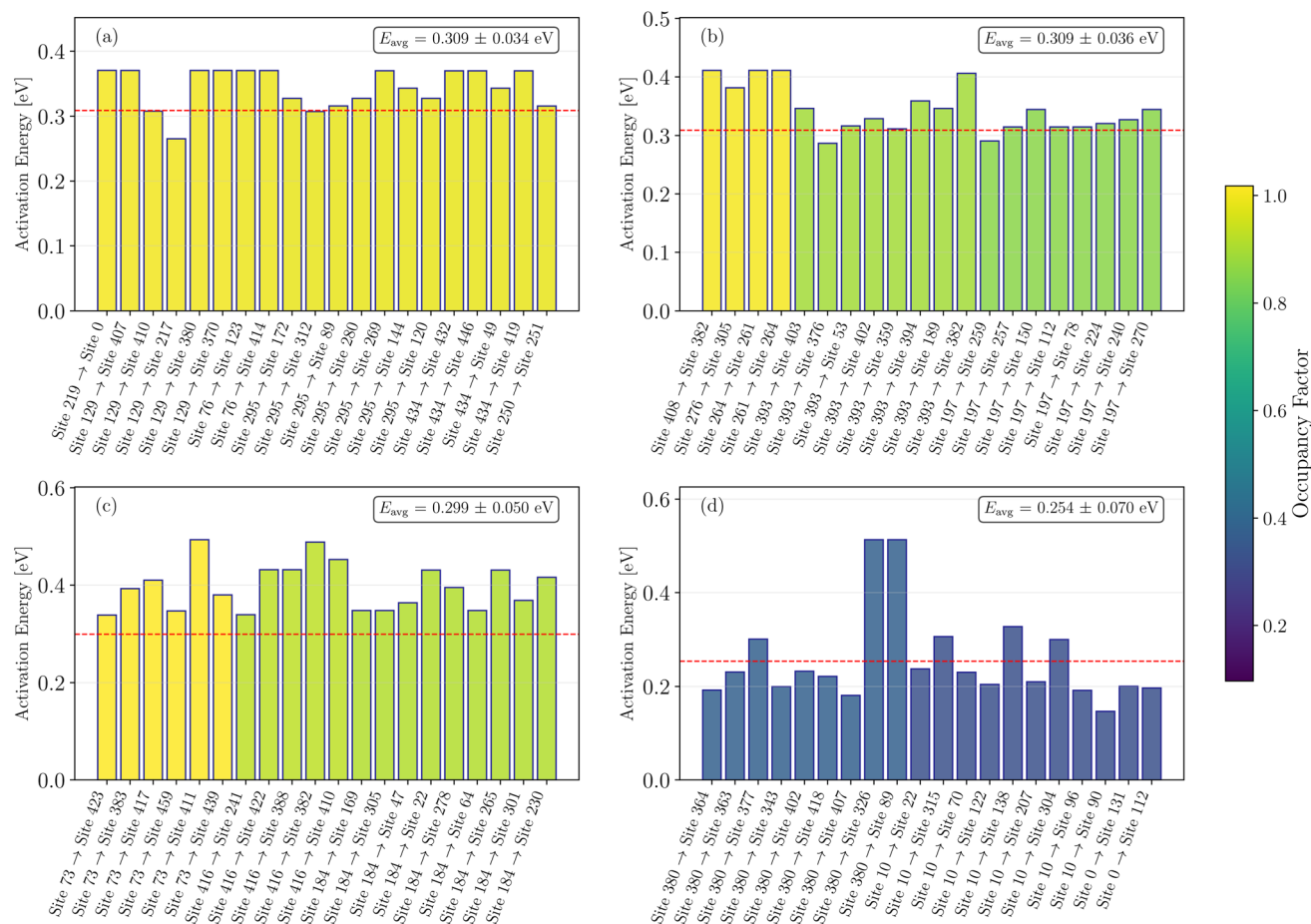


Fig. 4 Spectral distribution of the 20 highest individual activation energy barriers ($E_{a,i}$) derived from dynamic Li^+ -ion hopping statistics in glassy $\text{Li}_2\text{OHCl}_{0.5}\text{Br}_{0.5}$ at (a) 450 K, (b) 500 K, (c) 600 K, and (d) 700 K. The upper-right inset tracks the temperature dependence of the global ensemble-averaged activation barrier computed across all sampled hopping events, highlighting the activation of a low-energy pathway continuum at elevated temperatures.

occurring at times t_i and t_j is defined as correlated if it satisfies two simultaneous conditions:

$$\Delta t_{ij} = |t_i - t_j| \leq \tau_{\text{corr}}$$

$$d_{ij} = \|\mathbf{r}_i(t_i) - \mathbf{r}_j(t_j)\|_{\text{MIC}} \leq 10 \text{ \AA}$$

where $\tau_{\text{corr}} = \nu_{\text{attempt}}^{-1}$ (≈ 0.3 ps) represents the characteristic lattice relaxation time following a structural perturbation, and d_{ij} is the inter-site distance evaluated under the minimum-image convention. The 10 Å spatial cutoff encompasses all possible coordination spheres, capturing direct short- and medium-range inter-ionic coulombic interactions and localized lattice-strain field perturbations while excluding uncorrelated long-range thermal fluctuations. Self-pair events ($i = j$) are excluded by construction to ensure that the correlation metric isolates genuine multi-body transport processes. As plotted in Fig. S11, pairwise Li^+ - Li^+ displacement correlations persist across all investigated temperatures, peaking distinctly at 500 K—mirroring the maximum in structural and configurational heterogeneity previously identified *via* TAOG analysis. Interestingly, while the absolute frequency of multi-ion-correlated

events continues to increase at higher temperatures, it does not scale monotonically with the overall lithium-ion conductivity. This discrepancy demonstrates that the remarkable superionic performance of the glassy phase is not primarily driven by highly correlated or cooperative multi-particle string mechanisms. Instead, lithium transport within this mixed-halide antiperovskite glass is dominated by largely independent, thermally activated hopping events through a dynamically evolving, structurally adaptive network of stable and metastable sites.

3.5 Phonon landscapes and lattice softening mechanisms

Lattice dynamics, driven by the composition and spatial arrangement of atomic groups within a solid framework, govern macroscopic ion transport *via* lattice softening. Mechanistically, more compliant frameworks lower the structural resistance to local shear, effectively reducing the transient activation barriers for cation migration and accelerating ionic conductivity.^{49,89} To elucidate these lattice dynamical features, the temperature-dependent, species-projected vibrational density of states (VDOS) was extracted by taking the Fourier transform

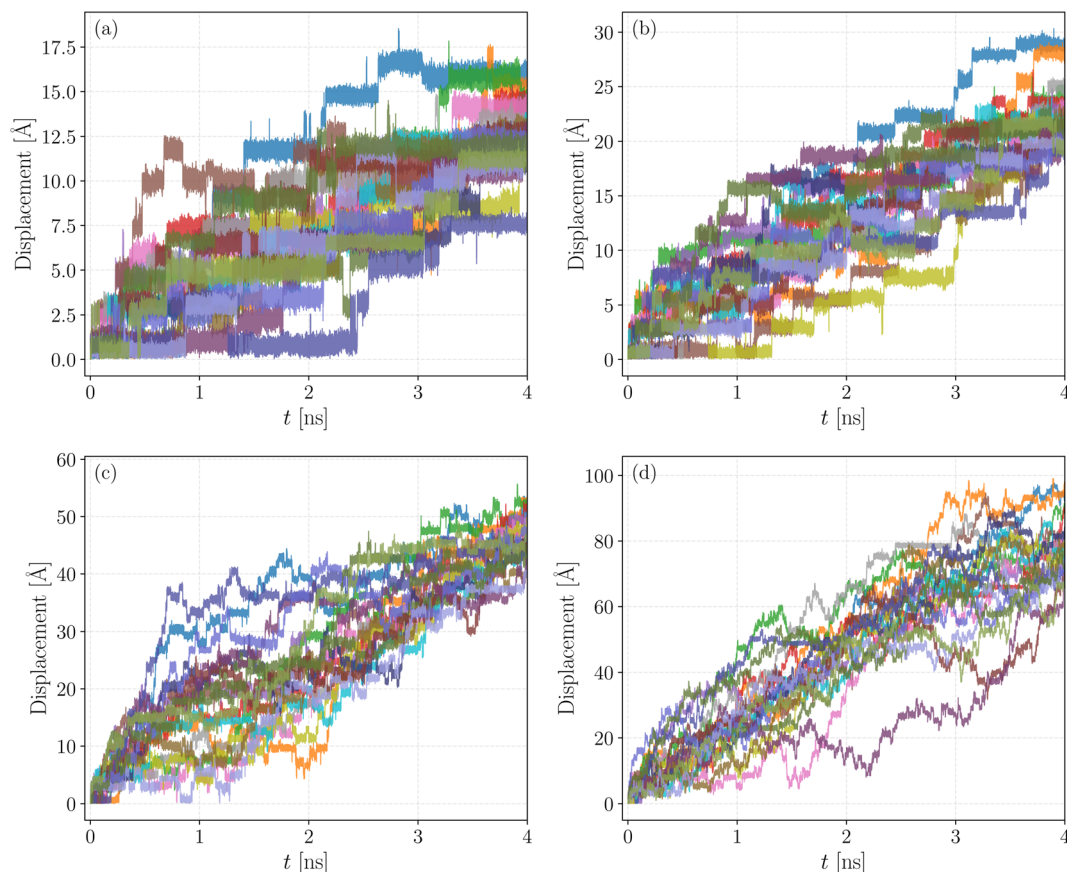


Fig. 5 Temporal evolution of individual atomic displacements for the 20 most mobile Li^+ ions in $\text{Li}_2\text{OHCl}_{0.5}\text{Br}_{0.5}$ glass at (a) 450 K, (b) 500 K, (c) 600 K, and (d) 700 K. The discrete, step-like transitions illustrate classical hopping-mediated transport between localized cages, with the residence time at structural plateaus systematically decreasing with increasing thermal activation.

of the velocity autocorrelation functions (VACFs) along the molecular dynamics trajectories (Fig. 6). For structural comparison, we used the static phonon density of states of the crystalline phase calculated using the trained potential (Fig. S2). The static phonon density of states exhibits a distinct zero-DOS frequency interval followed by a steep increase at higher energies, corresponding to a genuine phonon band gap that separates the low- and intermediate-frequency acoustic/optical

framework modes involving Li, O, and the halide species from the isolated, high-frequency localized modes dominated by light H atoms associated with O–H stretching and bending. This well-separated vibrational structure arises from the significant mass disparity and distinct force constants of the constituent species within the harmonic approximation. The steep onset at the lower edge of the high-frequency band reflects a high density of states concentrated within a narrow frequency range,

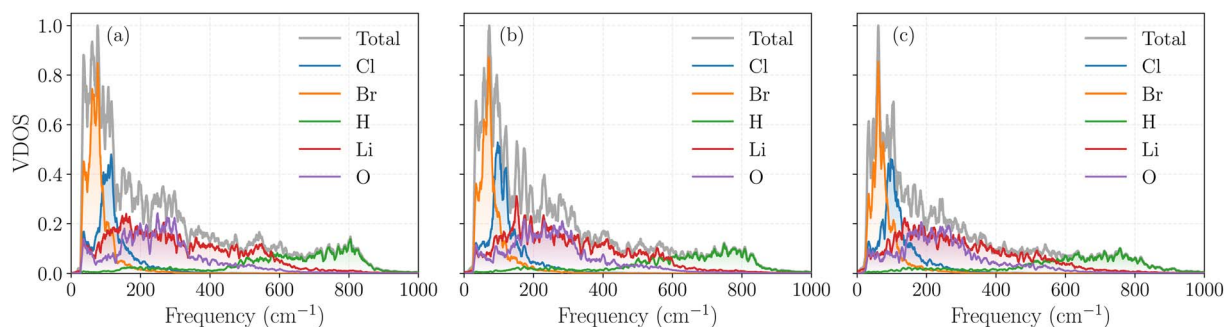


Fig. 6 Total and species-projected vibrational density of states (VDOS) of glassy $\text{Li}_2\text{OHCl}_{0.5}\text{Br}_{0.5}$ at (a) 500 K, (b) 600 K, and (c) 700 K, derived from the Fourier transform of the atomic velocity autocorrelation functions (VACFs). The concentration of Br-related modes below 100 cm^{-1} relative to Cl-modes signifies an overall softening of the structural framework, while the distinct spectral overlap between Li^+ and OH^- bands indicates strong localized dynamical coupling.

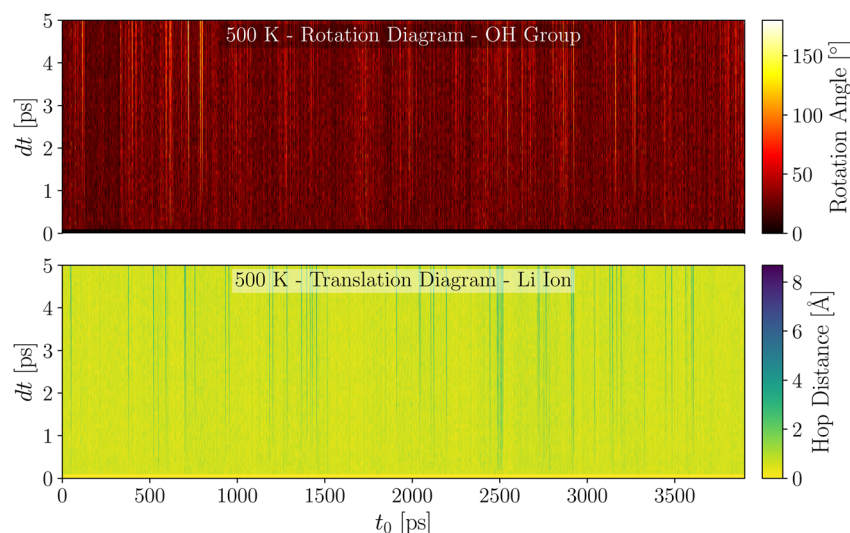


Fig. 7 Time-resolved correlation between polyanion rotation and cation translation in glassy $\text{Li}_2\text{OHCl}_{0.5}\text{Br}_{0.5}$ at 500 K. (Top) contour map tracking individual OH^- minimum angular displacements, where the low-angle background represents localized librations and the sharp, high-intensity streaks signify large-angle transient rotations. (Bottom) coincident translational displacement profile of the Li^+ ions, illustrating the tight temporal synchronization between successful site-to-site cation hops and large-angle hydroxyl reorientations.

characteristic of localized, weakly dispersing high-frequency modes sampled on a finite reciprocal-space grid.

The calculated VDOS profiles reveal distinct spectral partitioning based on the local mass and bonding environments of the anion sublattice. Vibrational modes associated with the heavier, more polarizable Br^- ions are predominantly localized below 100 cm^{-1} , whereas the lighter Cl^- modes occur primarily above 100 cm^{-1} . This distinct shift of the acoustic and low-frequency optical branches toward lower energies provides a direct signature of chemical lattice softening induced by bromide substitution. The presence of the larger halide species dilutes the internal lattice-restoring forces, yielding a highly compliant structural framework that lowers the steric resistance to local Li^+ hops. Furthermore, a significant spectral overlap is observed between the intermediate-frequency Li^+ vibrational bands and the lower-frequency librational modes of the OH^- hydroxyl groups (Fig. S12). This resonant alignment indicates a strong dynamical coupling between long-range lithium-ion transport and localized hydroxyl reorientations. Such coupled dynamics suggest that OH^- librational modes do not act merely as static structural spectators; instead, they participate in a cooperative, time-dependent modulation of the local electrostatic and potential energy landscapes, transiently smoothing out the migration pathways to promote superionic transport.

It is important to distinguish the Li^+ vibrational spectrum in Fig. 3 from the species-projected VDOS in Fig. 6. Fig. 3 is obtained from directional displacement turnarounds of caged Li^+ ions, isolating intra-cage rattling dynamics and providing the characteristic average attempt frequencies prefactor ($\nu_{\text{attempt}} \approx 3.22\text{--}3.43 \times 10^{12}\text{ s}^{-1}$) used in the dynamic hopping kinetics (eqn (4)). In contrast, Fig. 6 represents the conventional species-projected VDOS derived from the Fourier transform of atomic VACFs over the complete trajectories. While Fig. 3 serves to quantify localized attempt frequencies for hop-rate modeling,

Fig. 6 characterizes overall lattice dynamics, soft-mode distributions, and spectral coupling between Li^+ translational modes and host framework (OH^- , Cl^- , Br^-) motions.

3.6 Rotational-translational coupling and event correlation analysis

To uncover the direct atomistic relationship between polyanion dynamics and cation transport, we performed concurrent, event-resolved rotational and translational tracking along the molecular dynamics trajectories. Hydroxyl reorientational angles are evaluated reference-free as the minimum angular change of the O–H unit bond vector over a rolling window ($\Delta t = 5\text{ ps}$), $\theta = \arccos[\hat{\mathbf{u}}_{\text{OH}}(t_0) \cdot \hat{\mathbf{u}}_{\text{OH}}(t_0 + \Delta t)]$, rather than relative to fixed Cartesian axes. Concurrently, Li^+ displacements are calculated relative to instantaneous coordinates at t_0 , defining a hop *via* a $3\text{ \AA}$ inter-cage threshold. This event-correlation protocol does not assume permanently bound $\text{Li}^+\text{--OH}^-$ pairs over extended migration; rather, it tracks transient coordination environments, confirming that local polyanionic rotational excitations precede displacement hops to dynamically facilitate Li^+ transport across the disordered network. This dual event-detection approach maps out the raw temporal evolution, magnitude, and spatial characteristics of individual atomic rearrangements without the smoothing artifacts introduced by conventional time- or space-averaging. The trajectories in Fig. 7 present event-resolved profiles tracking individual Li^+ hopping events and local OH^- reorientational dynamics to illustrate their temporal coincidence, while broad statistical behavior across all populations is captured *via* ensemble averages in Fig. 8 and 9.

In the resulting correlation profiles (Fig. 7), the color intensity encodes the magnitude of change across the rolling time window. In the hydroxyl sublattice, the diffuse, low-angle

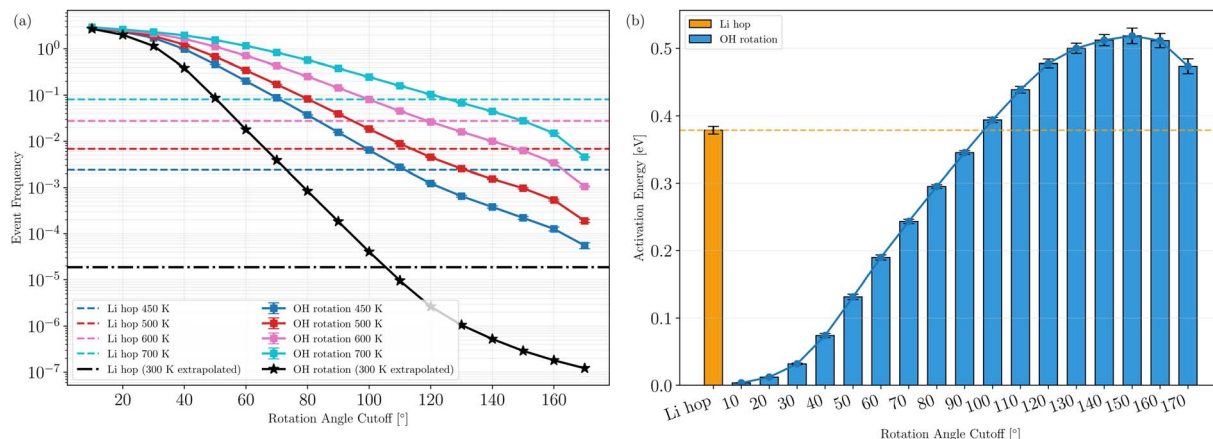


Fig. 8 Kinetic and energetic correlation between cation migration and polyanion rotation. (a) Arrhenius plots of Li^+ hopping frequencies (horizontal dashed lines) compared against discrete OH^- rotational event frequencies (solid circles) partitioned by angular cutoffs, with solid lines representing fits extrapolated to 300 K. Error bars denote standard errors calculated via poisson statistics. (b) Arrhenius-derived activation energies (E_a) for lithium transport steps (orange) contrasted against the angular-dependent activation barriers of the hydroxyl sublattice (blue), illustrating the energetic convergence near a 100° rotational angle.

background indicates continuous librational motion, characterized by rapid, small-amplitude wobbling within local potential wells. Rising above this baseline are sharp, sawtooth-like features that represent large-angle rotational excursions. At 500 K, intermittent large-angle OH^- reorientations approaching $\sim 170^\circ$ emerge periodically, with a prominent initial event resolved near $t_0 \approx 50$ ps. These events manifest as narrow, high-angle streaks that span only a brief temporal interval, revealing transient rotational excursions where the hydroxyl group quickly returns to its original orientation rather than undergoing a permanent structural inversion. The recurrence of these sharp features demonstrates that dynamically activated rotational fluctuations are superimposed onto the continuous low-frequency librational background.

Analogously, in the lithium transport profile, sharp sawtooth-like spikes track successful site-to-site hopping

events, while the low-intensity baseline captures localized rattling about equilibrium coordinates. Directly comparing the temporal alignment of these two distinct signals reveals that numerous Li^+ ion hops occur in immediate coincidence with large-angle OH^- rotations ($>160^\circ$). This striking synchronization indicates a powerful temporal association between net cation migration and localized polyanionic reorientation, suggesting that OH^- rotational modes actively modulate the local potential energy landscape to assist adjacent lithium transport. As the temperature is raised to 600 and 700 K (Fig. S13), both the frequency of these large-angle hydroxyl rotations and the rate of lithium-ion hopping accelerate dramatically. Crucially, their temporal coincidence becomes even more pronounced at these elevated temperatures. This behavior strongly supports a thermally cooperative transport model wherein rapid OH^- reorientations transiently dilute local steric and electrostatic

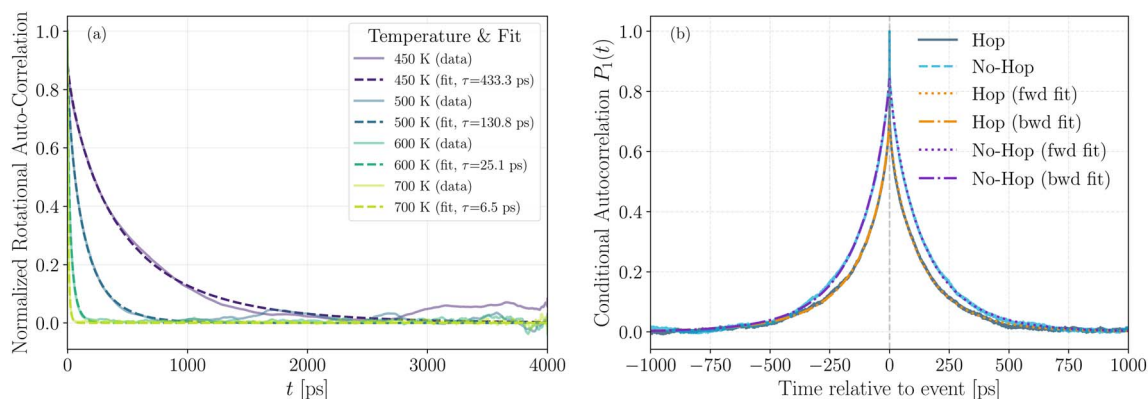


Fig. 9 Rotational autocorrelation function (RACF) analysis of OH^- groups in glassy $\text{Li}_2\text{OHCl}_{0.5}\text{Br}_{0.5}$. (a) Global, temperature-dependent RACF decays calculated over the full 4 ns production trajectories, where solid lines represent MD data, dashed lines denote exponential fits, and labels indicate the extracted relaxation time constants (τ). (b) Conditional first-order RACF profiles computed at 500 K for the local "Hop" ensemble (surrounding active Li^+ ions) and the "No-Hop" ensemble (surrounding stationary Li^+ ions) tracking backward ($t < 0$) and forward ($t > 0$) times relative to the hopping event ($t = 0$). The accelerated decay in the "Hop" environment confirms the presence of localized rotational-translational coupling.

barriers, opening wide, low-energy coordination pathways that facilitate frequent cation hopping and drive the superionic conductivity of the mixed-halide glass.

3.7 Kinetic mismatch and the partial paddlewheel mechanism

To quantitatively assess the cooperative link between cation translation and polyanion reorientation, we extracted the empirical activation barriers and absolute frequencies associated with these discrete events using a fine grid of spatial and angular thresholds (Fig. 8). Cation hopping was tracked using a fixed spatial displacement cutoff of 3 Å, while OH[−] reorientations were systematically partitioned using angular thresholds spaced at 10° increments. Both dynamical processes were integrated over a rolling observation window of $\Delta t = 1$ ps, selected to match the characteristic optical phonon and librational timescales identified in our VDOS analysis. This window size aligns with established statistical tracking protocols for superionic solid-state conductors;^{90,91} narrower time frames risk underestimating physically meaningful trajectories, whereas broader windows can artificially aggregate consecutive, independent transport steps.

Discrete atomic movements were identified from raw displacement trajectories using an automated peak-finding algorithm. An event was logged whenever a peak magnitude exceeded the specified distance or angular cutoff with a peak prominence of at least 50% of that threshold. Computing these counts across the production trajectories yielded explicit event frequencies (f) at 450, 500, 600, and 700 K, with statistical uncertainties modeled *via* Poisson statistics. The temperature dependence of these frequencies was modeled using the Arrhenius relation:

$$f(T) = A \exp\left(-\frac{E_a}{k_B T}\right) \quad (5)$$

where A is the pre-exponential frequency factor. Apparent activation energies were extracted from the slopes of $\ln(f)$ versus $1/T$, allowing for a direct, high-confidence extrapolation of individual channel kinetics to room temperature (300 K). Within this 1 ps observation window, large-angle OH[−] rotational events were detected up to an angular threshold of approximately 170°, whereas complete, idealized 180° flips were entirely absent (Fig. 8a). While both the Li⁺ hopping and OH[−] rotational frequencies scale monotonically with temperature by one to two orders of magnitude between 450 and 700 K, a severe kinetic mismatch exists between the two sublattices. Across the simulated temperature range, lithium transport steps occur roughly 18–44 times more frequently than large-angle hydroxyl rotations. When extrapolated to ambient conditions (300 K), this disparity expands to nearly two orders of magnitude, with lithium hops outpacing large-angle rotations by a factor of ~153. Consistent with this behavioral divergence, the apparent activation energy for large-angle OH[−] reorientations is significantly higher than that of lithium migration (Fig. 8b). This substantial disparity in both energetic barriers and raw frequencies strongly argues against a classical, fully

synchronized “paddlewheel” mechanism, which fundamentally requires comparable translational and rotational timescales to drive the mobile ions.

Nevertheless, as shown in Fig. 8b, OH[−] rotational excursions bounded near moderate angles (~100°) exhibit an activation energy profile that perfectly converges with the bulk migration barrier of the Li⁺ ions, highlighting the kinetic alignment between localized polyanionic reorientations and cation transport across the amorphous network. This energetic parity indicates that moderate-angle hydroxyl wobbling or partial reorientations occur on a timescale highly compatible with cation transport. Conversely, the activation barrier rises steeply as the angular threshold widens, confirming that large-angle OH[−] reorientations contribute negligibly to net charge transport. These findings substantiate a modified, partial paddlewheel mechanism within the amorphous matrix. In this framework, the continuous, low-barrier librational fluctuations and moderate-angle reorientations of the OH[−] groups are sufficient to dynamically expand the adjacent halide bottlenecks and lower local electrostatic repulsion, facilitating fast lithium transport without the energetic penalty of complete polyanionic inversion.

To assess the generalizability of the partial paddlewheel mechanism, it is important to clarify that its onset does not require a rigid, global threshold of amorphization. Rather than depending on a specific degree of long-range structural disorder, the mechanism is governed by local dynamic criteria: (i) local coordination heterogeneity that generates accessible metastable Li⁺ sites, (ii) local lattice compliance, and (iii) low-barrier, thermally accessible polyanion dynamics. Because localized, moderate-angle OH[−] librations (~100°) exhibit barrier-lowering effects comparable to full rotational flips, complete structural amorphization or long-range rotational synchronization is unnecessary. Therefore, this partial paddlewheel coupling represents a generalizable transport phenomenon applicable to a broader spectrum of antiperovskite solid electrolytes featuring local structural distortions and rotational polyanions, spanning from partially disordered crystalline phases to glassy networks.

3.8 Rotational relaxation and conditional ensemble analysis

To complement the discrete event-based tracking and comprehensively map out the continuous orientational dynamics of the polyanion sublattice, we evaluated the first-order rotational autocorrelation function (RACF):

$$C_1(t) = \langle P_1[\hat{\mu}(0) \cdot \hat{\mu}(t)] \rangle \quad (6)$$

where $\hat{\mu}$ represents the OH[−] bond unit vector and $P_1(x) = x$ is the first-order Legendre polynomial. Unlike threshold-dependent peak counting, the RACF captures the entire spectrum of orientational decorrelation, including fast high-frequency librations, partial wobbling, and large-angle inversion steps. The characteristic rotational relaxation lifetime (τ) was extracted *via* exponential decay fitting, defining the effective macro-rotational frequency as $f_{\text{rot}} = 1/\tau$.

Table 3 Comparison of ensemble-averaged OH[−] rotational frequencies derived from RACF decay constants (τ) and corresponding Li⁺-ion hopping frequencies across the investigated temperature range

Temperature (K)	OH rotational frequency (THz)	Li hopping frequency (THz)
450	0.00231	0.00241
500	0.00765	0.00682
600	0.03984	0.02757
700	0.15419	0.08109

As illustrated in Fig. 9a, the RACF profiles decay progressively faster with increasing temperature, tracking the thermal activation of the polyanionic network. The extracted relaxation times steadily contract, corresponding to a sharp increase in the effective OH[−] rotational frequencies (Table 3). Comparing these metrics directly with net lithium-ion hopping frequencies reveals that both localized sublattices accelerate in step as thermal energy increases. However, the RACF-derived OH[−] rotational frequencies remain consistently higher than the corresponding lithium transport rates. This divergence becomes highly pronounced at elevated temperatures (*e.g.*, 0.154 THz *versus* 0.081 THz at 700 K). This frequency offset is a direct consequence of what each technique captures: the RACF registers continuous, multi-scale orientational decorrelation averaged over all hydroxyl groups—including rapid, non-diffusive librations—whereas the lithium frequency isolates discrete, successful translational hops across high-energy cage boundaries. This distinct timescale mismatch reinforces our earlier conclusion that transport is not governed by a rigid, fully synchronized paddlewheel mechanism. Instead, it points toward a cooperative framework in which high-frequency, continuous local OH[−] fluctuations lower the local activation energy barriers to assist independent lithium transport steps.

To establish that Li⁺ migration is locally facilitated by adjacent polyanionic dynamics rather than spatially decoupled coincidences, a spatially resolved conditional RACF analysis was conducted around individual hopping events (Fig. 9b). This conditional rotational autocorrelation analysis focused around individual cation migration events ($t = 0$). Lithium hops were defined as a spatial displacement exceeding 3.0 Å within a 1 ps time step. For every successful hop, all hydroxyl groups residing within a first-shell radius of 3.5 Å from the migrating cation were assigned to a local “Hop” ensemble. Concurrently, an identical population of hydroxyl groups centered around non-migrating, caged lithium ions was isolated to serve as a baseline “No-Hop” preference ensemble. The conditional RACF was then tracked for both local environments across a wide time window spanning −1000 ps to +1000 ps relative to the precise instant of the hop. Within this framework, the backward-time domain ($t < 0$) monitors the preparatory lattice dynamics preceding a hop, while the forward-time domain ($t > 0$) records the post-event structural relaxation of the amorphous coordination cage.

Fig. 9b details the resulting conditional RACF curves evaluated at 500 K. The local “Hop” ensemble displays a distinctly

accelerated orientational decorrelation compared to the stationary “No-Hop” reference in both the forward and backward directions. This trend indicates that the hydroxyl groups directly surrounding an active transport channel are significantly more dynamically active than those in the rest of the glassy matrix. Exponential fits to these localized decay slopes yield relaxation time constants of $\tau_{\text{Hop}}^{\text{bwd}} = 118.9$ ps and $\tau_{\text{Hop}}^{\text{fwd}} = 123.2$ ps, representing a visible contraction relative to the reference baseline values ($\tau_{\text{No-Hop}}^{\text{bwd}} = 136.6$ ps and $\tau_{\text{No-Hop}}^{\text{fwd}} = 136.7$ ps).

Crucially, this acceleration in the “Hop” ensemble is already well established in the backward-time domain ($t < 0$). This pre-event decay reveals that localized polyanionic rotational excitation develops prior to the actual translation step, functioning as a dynamic catalyst that transiently distorts the local electrostatic field and widens the structural bottleneck, thereby lowering the migration barrier. The persistence of this accelerated relaxation into the forward-time domain ($t > 0$) indicates that the local coordinate cage remains structurally excited immediately following the cation's departure, slowly dissipating its excess kinetic energy back to the equilibrium amorphous network. While these findings offer direct, unambiguous evidence of localized rotational-translational coupling, the relatively modest difference between the “Hop” and “No-Hop” profiles confirms that complete polyanionic inversion is not a mandatory prerequisite for cation migration. Instead, these results solidify the partial paddlewheel mechanism: long-range lithium transport is driven by independent, thermally activated hops that are locally facilitated and smoothed by continuous, moderate-angle reorientations of the surrounding hydroxyl framework.

Our conditional autocorrelation and event-based tracking demonstrate that cation migration in glassy Li₂OHCl_{0.5}Br_{0.5} does not require a fully synchronized, traditional paddle-wheel inversion. Instead, continuous moderate-angle hydroxyl librations and localized lattice compliance transiently dilate bottleneck channels. This behavior represents a dynamic regime intermediate between conventional phonon-assisted hopping in rigid crystalline frameworks⁸⁸ and the liquid-like, relaxational transport dynamics recently observed in highly disordered superionic conductors⁹²

It is important to contextualize the role of OH[−] rotational dynamics in the glassy antiperovskite framework relative to that in its crystalline counterparts. In crystalline Li₂OHCl, OH[−] rotational disorder is well-documented to enhance Li⁺ mobility *via* paddlewheel-type coupling.^{45,48} In the present glassy matrix, however, ion transport does not require a classical, globally synchronized paddlewheel process. Instead, our multi-level dynamic analyses – encompassing temporal event tracking, vibrational spectrum coupling, and conditional relaxation functions – demonstrate a partial paddlewheel mechanism. Localized OH[−] librations and moderate-angle reorientations (~100°) act as local kinetic facilitators by transiently lowering migration barriers and expanding bottleneck dimensions. Consistent with this interpretation, a control simulation at 600 K with frozen OH[−] units yields a pronounced reduction in the Li⁺ MSD and a drastic drop in ionic conductivity—from 2.47 ×

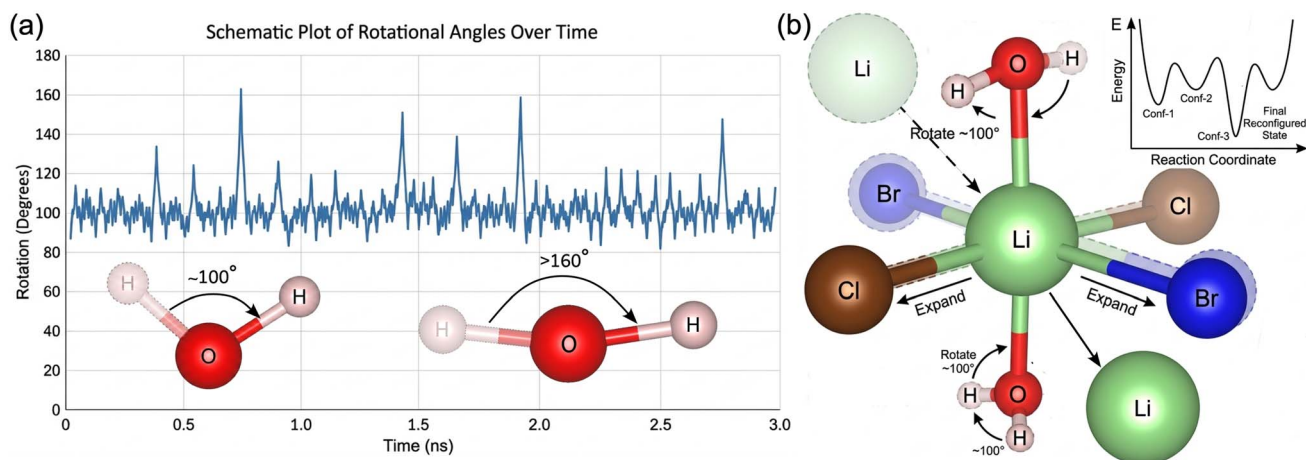


Fig. 10 Schematic illustration of the partial paddlewheel mechanism. (a) Angular trajectories of OH[−] showing moderate-angle librations (~100°) and large-angle reorientations (>160°). (b) Stepwise coupling of local OH[−] reorientation with Li⁺ migration, where transient coordination changes and bottleneck widening facilitate Li⁺ hopping, followed by framework relaxation.

10^{-1} to $8.01 \times 10^{-4} \text{ S cm}^{-1}$ – relative to the fully dynamical amorphous $\text{Li}_2\text{OHCl}_{0.5}\text{Br}_{0.5}$ framework (Fig. S14). These results clearly demonstrate that OH[−] dynamics actively facilitate Li⁺ transport. Consequently, polyanion motion in the amorphous phase acts as an opportunistic, facilitating component of the transport landscape rather than a fully synchronized paddlewheel mechanism.

Fig. 10 provides a schematic illustration of the multiscale kinetic analysis and the proposed partial paddlewheel mechanism. The top panel explicitly illustrates the angular trajectory of the OH[−] polyanion, highlighting the large number of localized, moderate-angle librations (~100°), whose activation energy is comparable to that of Li⁺ migration, as well as the large-angle reorientations (>160°) relative to the surrounding lattice matrix. Panel (b) depicts the stepwise coupled transport mechanism, illustrating how local and unsynchronized OH[−] reorientations transiently modify the Li⁺ coordination environment and widen the surrounding halide bottleneck, facilitating Li⁺ transfer between neighboring cages by locally smoothing the heterogeneous migration landscape. Following the hop, the local framework relaxes toward a new metastable configuration. This sequence defines a partial paddlewheel mechanism, where OH[−] rotational fluctuations assist Li⁺ migration without requiring synchronized or complete periodic 180° rotations for individual transport events.

4 Conclusions

In summary, we have developed a highly accurate and transferable deep neural network interatomic potential within the DP-GEN active-learning framework to systematically investigate the superionic conduction mechanisms in mixed-halide antiperovskite ($\text{Li}_2\text{OHCl}_{0.5}\text{Br}_{0.5}$) glasses. By combining near-first-principles accuracy with large-scale molecular dynamics simulations, this machine-learning potential overcomes the length- and timescale limitations inherent to conventional *ab initio* approaches, providing an explicit dynamical picture of ion

transport across a broad thermodynamic range. Our findings reveal that the exceptional room-temperature ionic conductivity ($\sim 2.43 \times 10^{-4} \text{ S cm}^{-1}$) and low macroscopic activation energy (0.35 eV) of the glassy phase originate from a combination of structural, lattice-dynamical, and polyanionic factors:

- **Topological heterogeneity:** time-averaged occupancy grid (TAOG) analysis demonstrates that amorphization introduces a high density of distortion-induced, metastable lithium environments that coexist alongside parent-topology-associated environments. This structural disorder establishes a spatially rugged yet continuous percolation network characterized by a broad distribution of local migration barriers. The population of these dynamically accessible coordination environments maximizes near 500 K, capturing a peak in configurational heterogeneity that correlates remarkably well with experimental differential scanning calorimetry benchmarks.

- **Lattice softening:** vibrational density of states analysis shows that chemical substitution with the larger, more polarizable Br[−] anion shifts the acoustic and low-frequency optical phonon branches downward. This localized lattice softening dilutes internal restoring forces, rendering the framework more compliant and reducing the steric resistance encountered by transiting Li⁺ ions through the halide bottlenecks.

- **Rotational-translational coupling:** comprehensive event-detection tracking, rotational autocorrelation function analysis, and localized conditional ensemble modeling provide unambiguous, quantitative evidence of synchronization between polyanionic and cationic sublattices. Cations residing within active transport channels experience an accelerated local OH[−] rotational decorrelation. Crucially, this polyanionic excitation is established prior to the actual translation step ($t < 0$), demonstrating that local hydroxyl fluctuations act as dynamic facilitators that transiently reshape the local potential energy landscape and lower the instantaneous migration barrier.

Importantly, our multi-scale kinetic analysis rules out a classical, fully synchronized “paddlewheel” mechanism. The massive numerical mismatch between the absolute frequencies

of long-range lithium hops and large-angle hydroxyl rotations – spanning nearly two orders of magnitude when extrapolated to room temperature – confirms that complete 180° polyanionic inversions are too energetically demanding to serve as mandatory transport prerequisites. Instead, we propose a refined partial paddlewheel mechanism: lithium transport is dominated by independent, thermally activated hops that are locally facilitated and smoothed by continuous, low-barrier librational wobbling and moderate-angle (~100°) reorientations of the surrounding hydroxyl framework.

By delivering a unified, atomistic view of how glassy disorder, compositional lattice softening, and partially coupled polyanionic dynamics synergistically govern fast-ion conduction, this work establishes a rigorous computational framework for analyzing disordered solid electrolytes. The insights gained offer clear design principles for optimizing solid-state ionic conductors, underscoring the potential of harnessing structural amorphization and localized polyanionic rotation to develop next-generation energy storage materials.

Author contributions

AM and RS conceived the problem. RS conducted all the simulations. RS and AM analyzed the results and prepared the draft.

Conflicts of interest

There are no conflicts to declare.

Data availability

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

Supplementary information (SI): deep learning potential training curves, simulated XRD patterns, partial radial distribution functions, proton mean squared displacements, 3D volumetric time-averaged occupancy grid (TAOG) maps, lithium-ion vibrational amplitude distributions, vibrational reference spectra for pure Li₂OHCl and Li₂OHBr, multi-ion collective hopping correlation metrics, harmonic phonon density of states (DOS) profiles, deconvoluted species-projected VDOS overlays, and time-resolved event-correlation maps at supplementary temperatures. See DOI: <https://doi.org/10.1039/d6ta05828k>.

Acknowledgements

The authors gratefully acknowledge the Indian Institute of Technology Gandhinagar, India, for providing research facilities and financial support. We thank PARAM Ananta for computational resources.

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