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Authors

Sun, Yingzhi

Ouyang, Bin

Wang, Yan

et al.

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Enhanced ionic conductivity and lack of paddle-wheel effect in pseudohalogen-substituted Li argyrodites

Author List:

Yingzhi Sun,^{1,2,6} Bin Ouyang,^{1,2,3,6} Yan Wang,⁴ Yaqian Zhang,² Shuo Sun,⁵ Zijian Cai,^{1,2} Valentina Lacivita,⁴ Yinsheng Guo,⁵ and Gerbrand Ceder^{1,2,7,*}

¹ Department of Materials Science and Engineering, University of California Berkeley, Berkeley, CA 94720, USA

² Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

³ Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306, USA

⁴ Advanced Materials Lab, Samsung Advanced Institute of Technology-America, Samsung Semiconductor, Inc., Cambridge, MA 02138, USA

⁵ Department of Chemistry, University of Nebraska-Lincoln, Lincoln, NE 68526, USA

⁶ These authors contributed equally

⁷ Lead Contact

* Correspondence: gceder@berkeley.edu

SUMMARY

Superionic conductors are key to the development of safe and high-energy-density all-solid-state batteries. Using a combined theoretical and experimental approach, we explore the feasibility of increasing the ionic conductivity through pseudohalogen substitution in the Li argyrodite structure. Under the guidance of calculated thermodynamic stability, BH_4 -substituted Li argyrodite, $\text{Li}_{5.91}\text{PS}_{4.91}(\text{BH}_4)_{1.09}$, was successfully synthesized via a mechanochemical method. As-synthesized BH_4 -substituted Li argyrodite displays an ionic conductivity of 4.8 mS/cm at 25 °C. Ab initio molecular dynamics simulation trajectory analysis was used to investigate how BH_4 facilitates Li-ion diffusion and indicates only a weak correlation with the B-H bond motion. We find that the enhanced conductivity mainly originates from the weak interaction between Li and BH_4 and find no evidence of a paddle-wheel effect from the polyanion. This work provides insight on how cluster ions enhance Li diffusion and systematically describes how to explore superionic conductors with pseudohalogen substitution.

1. INTRODUCTION

The application of solid-state electrolytes provides opportunities for batteries that are safer and more powerful than current state-of-the-art Li-ion batteries.^{1,2} Driven by the demands for solid-state electrolytes, there has been a rapidly growing interest in the discovery of solid-state alkali ionic conductors with ionic conductivities equal to or higher than those of liquid electrolytes.³⁻⁹

Although most recent work for improving ionic conductivity has focused on substituting cation sites,⁹⁻¹² less work has been done on modifying the anion chemistry though their framework is known to be important for ionic conductivity.⁸ In this paper we focus on cluster-ion substitution as it provides an option for engineering the anion framework. Compared with single-ion substitution, cluster-ion substitution provides more degrees of freedom including bond stretching and bond bending, which may assist alkali-metal to preserve their coordination as much as possible as they migrate through the transition state, a factor which is important in the migration of many cations.^{8,13} To date, it remains unclear whether and how these additional degrees of freedom lead to higher conductivity, even though high conductivities have been reported in several recent studies.¹⁴⁻¹⁹ Specifically, several-orders-of-magnitude enhancement in the ionic conductivity has been reported in both theoretical and experimental work applying cluster-ion substitution in antiperovskite-type materials.¹⁷⁻¹⁹ The cluster ions used in those reports can be classified as pseudohalogen anions, as the formal charge of such cluster ions equals that of a halogen, and the strong covalent interactions within such a cluster ion cause it to behave as a unit. Considering the frequent appearance of

halogens in fast-ionic conductors, it is important to understand how pseudohalogen substitution influences ionic conductivity.

The argyrodite structure is a good framework to study the pseudohalogen effect as it already has reasonable conductivity with the presence of regular halogens.^{4,20-23} As the halogen site in argyrodite has only mobile Li⁺ in its first coordination shell, it is loosely bonded with the rest of the framework creating the expectation that it may be easier to substitute.^{3,24} The most widely studied argyrodites are derived from halogen substitution in the Li₇PS₆ argyrodite prototype, which yields various forms of Li₆PS₅Cl, Li₆PS₅Br, and Li₆PS₅I. Halogen substitution has been reported to have a beneficial effect on the diffusion of Li ions with the ionic conductivity of halogen-substituted argyrodite-type materials varying from 10⁻³ mS/cm to 10 mS/cm.^{4,24-29}

In this paper, we explore the feasibility of enhancing the ionic conductivity through pseudohalogen substitution in the Li argyrodite system using a combined theoretical and experimental approach including first-principles stability analysis, solid-state synthesis, structure characterization, and ab initio molecular dynamic (AIMD) analysis. A computational screening of potential Li argyrodite pseudohalides to determine the synthetically accessible argyrodite pseudohalides points at BH₄-substituted Li argyrodites as the most stable pseudohalides. An argyrodite-type material with the composition Li_{5.91}PS_{4.91}(BH₄)_{1.09} was successfully synthesized using a mechanochemical method and shown to have a high ionic conductivity of 4.8 mS/cm at room temperature, considerable higher than that of conventional halogen-substituted Li argyrodites.

When explaining the effect of polyanions/cluster anions on Li-ion diffusion, most recent work has centered on whether there is a synergistic effect between the polyanions and Li diffusion (the so-called "Paddle-Wheel" effect).^{16,19,30-32} Our theoretical analysis shows that the motion of Li ions has only a weak relationship with any motion of the BH_4 anion. Hence, rather than appealing to a "paddle-wheel" effect we argue that the enhanced conductivity mainly originates from the Li-pseudohalogen interaction which is weaker than the Li-halogen (Cl, etc.). As a result, Li ions are trapped for a shorter time near the pseudohalide groups and diffuse faster. This finding also indicates that the origin of higher conductivity in the argyrodite structure with pseudohalogen substitution is the flattening of the energy landscape with the introduction of light and highly covalent cluster ions, rather than any "dynamical coupling" between Li diffusion and polyanion rotation, as has been speculated in the literature. Our study provides a mechanistic understanding of how pseudohalogen substitution can help increase Li-ion conductivity, shedding light on design strategies for optimizing ionic conductivity by engineering the anion framework of conductors.

2. RESULTS

2.1. Crystal Structure and Phase Stability

The general (pseudo)halogen-substituted argyrodite is reported to have a crystal structure with cubic symmetry as shown in Figure 1A. Three crystallographic positions in the argyrodite structure, 4a, 4c, and 16e, are associated with sulfur ions. The 4b site is occupied by P which binds 4 S ions to it into a PS_4 group. In contrast, the 4a and 4c sites are occupied by S atoms which are relatively far away from all other non-Li atoms ($> 4 \text{ \AA}$) and are not considered to be part of a covalent bond complex. As a result, sulfur in the 4a and 4c sites is usually easier to substitute.²⁵

To understand the compositional range over which different Li argyrodite pseudohalides can exist, five pseudohalide ions were considered for substitution on 4a and/or 4c. Four types of substitution are considered, distinguished by their site occupancy (shown in Figure 1B). The first three types of substitution form Li_6PS_5X ($X = \text{halogen or pseudohalogen}$), which corresponds to the occupancy of a (pseudo)halogen on either the 4a or 4c site, or half occupancy on both the 4a and 4c sites. In the fourth type, both the 4a and 4c sites are fully substituted by the (pseudo)halogen, leading to the composition $Li_5PS_4X_2$ ($X = \text{halogen or pseudohalogen}$). To evaluate the energy of these compounds, we enumerated the 10 possible Li arrangements across the 48h sites (denoted as the Li site) and picked the one with lowest DFT energy. We did not consider possible occupancy of Li in other sites, such as 48h', 16e, and 24g because we find that the change in energy of our structures when moving a Li from 48h to 48h' is small (see Supplemental Table 1), and will therefore not significantly influence relative phase stability, but including it in all calculations would require unnecessarily large supercells.

For each Li-Vac configuration on the 48h sites, the S-(pseudo)halogen ordering with lowest electrostatic energy was selected for DFT calculations. The orientation of the pseudohalogen was initialized by rotating the pseudohalogen until the average interatomic distance between the cluster ions and the neighboring cations is maximized. The phase stability was evaluated by comparing the energy of the substituted argyrodites to that of all the possible combinations of competing phases (the convex hull construction).³³ Figure 1C shows that most argyrodites have non-zero energy above the convex hull (E_{hull}), indicating that at 0 K, they are not a thermodynamic ground state. However, the halide versions of the argyrodites, such as $\text{Li}_6\text{PS}_5\text{Cl}$ and $\text{Li}_6\text{PS}_5\text{Br}$, have been synthesized³, indicating that they can be stabilized by entropy, as is the case for other fast ion conductors,^{34,35} or that metastable synthesis pathways to their formation exist³⁶. It should be mentioned that we only use the E_{hull} values to indicate the relative stability of argyrodites with different (pseudo)halogen substitutions. An argyrodite with a low E_{hull} value does not necessarily guarantee synthetic accessibility. To give an example, $\text{Li}_5\text{PS}_4\text{X}_2$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) has never been reported experimentally in literature. This is consistent with a broad analysis of metastable compounds which indicates that while low E_{hull} is required for possible existence of metastable compounds, it is not a sufficient condition.³⁶

The phases that compete for phase stability for each argyrodite are given in Table 1. Most of these are stoichiometric phases, implying that they will not generate much configurational entropy at non-zero temperature, and hence will create more favorable conditions for the formation of the argyrodite at higher temperature.

Synthesis and Characterization

Our ab initio results indicate that BH_4 -substituted argyrodites have the lowest E_{hull} among the pseudohalogen substituted compounds, making them likely candidates for synthesis. In addition, Sakuda et al. recently reported that an argyrodite phase appeared in the $(100-x)(0.75\text{Li}_2\text{S} \cdot 0.25\text{P}_2\text{S}_5) \cdot x\text{LiBH}_4$ mixture with $x \geq 43$.³⁷ So, we set BH_4 -substituted argyrodites as our target materials. β - Li_3PS_4 , which is a metastable phase at room temperature, was used as precursor to increase the thermodynamic driving force for the formation reaction of the pseudohalide argyrodite. In addition, the Li_3PS_4 precursor has the PS_4 groups preformed, which may make it easier to form the argyrodite. Because LiBH_4 decomposes at high temperature,³⁸ a heating process is not suitable for this reaction. Instead, a mechanochemical method using high-energy ball milling (SpexSamplePrep 8000M Mixer/Mill, 1425 RPM) was used. To prevent the sample temperature from becoming too high, the ball milling was interrupted for 15 min after every 30-min milling. In addition, we find that excess LiBH_4 is necessary to the synthesis of BH_4 -substituted argyrodite since LiBH_4 is easily oxidized and consumed during the synthesis. When the precursors were mixed in the stoichiometric ratio of $\text{Li}_6\text{PS}_5\text{BH}_4$ (β - Li_3PS_4 : LiBH_4 : Li_2S = 1: 1 : 1), no argyrodite phase was formed in the product (Figure S1).

Synchrotron X-ray diffraction (XRD) (shown in Figure 2A) was conducted to confirm that an argyrodite phase was formed with a small amount (~2.8 wt %) of remaining LiBH_4 . The synchrotron XRD pattern was refined using the Rietveld method with the TOPAS V6 software package to determine the lattice parameters, atomic positions, and occupancies. The best fits were obtained when the BH_4^- and S^{2-} ions are assumed to be disordered over the 4a site and 4c site. As shown in Table 2, the refined B occupancies of the 4a and 4c sites are 0.584 and 0.506,

respectively, indicating that the chemical formula of the as-synthesized BH_4^- -substituted argyrodite is $\text{Li}_{5.91}\text{PS}_{4.91}(\text{BH}_4)_{1.09}$.

Transmission electron microscopy (TEM) electron diffraction (ED) patterns of the as-synthesized materials are presented in Figure 2B. The diffraction spots match with the calculated diffraction rings of the argyrodite structure, confirming the formation of the argyrodite phase. STEM energy dispersive spectroscopy (EDS) mapping images are presented in Figure 2C and indicate a homogeneous distribution of B throughout the particles, further corroborating the bulk substitution of BH_4^- .

To confirm the successful incorporation of the BH_4^- unit, we also measured the Raman response of the argyrodite electrolytes and their precursors. The BH_4^- internal stretching modes have characteristic frequencies residing in the 2200cm^{-1} to 2400cm^{-1} region, allowing for easy and unambiguous identification. As shown in Figure 2E, we observed the BH_4^- stretching modes in the $\text{Li}_{5.91}\text{PS}_{4.91}(\text{BH}_4)_{1.09}$ sample and in the LiBH_4 positive control compound, whereas in the $\beta\text{-Li}_3\text{PS}_4$ and $\text{Li}_6\text{PS}_5\text{Cl}$ negative control compounds, the BH_4^- stretching region is spectrally silent. The presence of the BH_4^- stretching modes provides further evidence that the BH_4^- is successfully incorporated into the argyrodite electrolyte.

2.2. Electrochemical Performance

Electrochemical impedance spectroscopy (EIS) measurements were performed to determine the ionic conductivity of the cold-pressed $\text{Li}_{5.91}\text{PS}_{4.91}(\text{BH}_4)_{1.09}$ with the results shown in Figure 3A and 3B. The impedance data was fit with an equivalent circuit consisting of one parallel constant phase element (CPE)/resistor in series with a CPE. In the $\text{Li}_{5.91}\text{PS}_{4.91}(\text{BH}_4)_{1.09}$

sample, the response of the CPE/resistor has shifted to frequencies that are too high to measure with the impedance analyzer, and only the tail of the blocking electrode was used for the fit. The EIS results indicate a room-temperature (RT) ionic conductivity of 4.8 mS/cm. This value is several orders of magnitude higher than that of the precursor β -Li₃PS₄ and LiBH₄ (Figure S2), ensuring that we did not measure the conductivity of the remaining β -Li₃PS₄ and LiBH₄ precursors. The EIS of Li_{5.91}PS_{4.91}(BH₄)_{1.09} at different temperatures are plotted in Figure 3B. The Arrhenius plots of the BH₄-substituted Li argyrodite (Li_{5.91}PS_{4.91}(BH₄)_{1.09}) and conventional halogen-containing Li argyrodite (Li₆PS₅Cl and Li₆PS₅Br) are compared in Figure 3C. The RT ionic conductivity of the BH₄-substituted Li argyrodite is ~5 times higher than that of Li₆PS₅Cl (0.95 mS/cm) and Li₆PS₅Br (0.87 mS/cm) and has a lower activation energy of 0.27 eV. The Li concentration of BH₄-substituted Li argyrodite is only slightly (1.5 %) lower than that of halogen-substituted argyrodites (Li₆PS₅Cl and Li₆PS₅Br), which cannot be responsible for the ~5-fold increase of ionic conductivity.³⁹ This result strengthens our argument that pseudohalogen substitution indeed improves the ionic conductivity of argyrodite-like compounds. To further evaluate the electrochemical performance of the BH₄-substituted Li argyrodite, a prototype all-solid-state cell was assembled with as-synthesized Li_{5.91}PS_{4.91}(BH₄)_{1.09}, an indium-metal anode, and a LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ cathode. On the cathode side, LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ was coated with lithium borate Li₃B₁₁O₁₈, which has been reported to protect the cathode from reaction with a sulfide electrolyte.⁴⁰ The cell was cycled between 1.4 and 3.7 V (2.0 and 4.3 V vs. Li/Li⁺) at a current density of 0.05 mA/cm² under room temperature. The cell was held at 3.7 V for 3 hours after charging. The first-cycle capacity loss of ~60 mAh/g is likely attributable to the decomposition of the solid electrolyte. As is common in sulfides,⁴¹

the excess charge capacity disappeared after the first cycle, indicating that a passivation layer may have formed at the interface between the electrolyte and carbon framework. A reversible capacity of ~130 mAh/g was obtained during the first two cycles (shown in Figure 3D). However, the capacity of this all-solid-state cell faded to 101 mAh/g after 10 cycles (as shown in Figure 3D and Figure S3) which may be attributed to the fact that a BH_4 group can be easily oxidized at high voltage.

3. DISCUSSION

Ab-Initio Molecular Dynamics (AIMD) can be an effective approach to understand how different local structures contribute to the overall conductivity, as it can probe the correlation between local Li hopping and polyanion dynamics. The AIMD trajectory in a period of 10 ps at 600 K was selected to visualize the correlation between Li diffusion and polyanion groups. The atomic trajectories of selected Li with one of its first neighboring BH_4 groups and PS_4 groups are illustrated in Figure 4A and 4B. Besides the Li migration observed in the trajectories, there is very significant BH_4 motion, such that the BH_4 trajectory almost fills the spherical space around it as shown in Figure 4A. In contrast, because there is relatively less movement in the PS_4 group, its trajectory remains a tetrahedron shape, as observed in Figure 4B for the PS_4 group. The structural dynamics of BH_4^- and PS_4^{3-} groups predicted by AIMD are consistent with Raman spectroscopy observations. Figure 2E shows that the BH_4^- characteristic stretching modes in the BH_4 argyrodite sample are significantly broadened, in contrast to the sharp and well-resolved modes in the LiBH_4 lattice. This marked increase in the linewidth indicates significant damping and frequent scattering in the vibrational trajectories of the BH_4^- group in

BH₄-argyrodite, which supports the AIMD result. On the other hand, as shown in Figure 2D, the PS₄³⁻ group characteristic mode at ~ 420cm⁻¹ largely maintains its narrow linewidth across the β-Li₃PS₄, Cl-argyrodite and BH₄-argyrodite. This behavior is consistent with the AIMD simulations showing well-defined small-amplitude vibrational motion of the PS₄³⁻ group. These observations indicate that BH₄ is very flexible and free to move locally in contrast with PS₄. That suggests the possibility that BH₄ may easily relax away when Li moves, thereby facilitating its hopping.

Given that BH₄ and PS₄ behave quite differently in terms of vibrational motion, one may expect that the BH₄ motion will facilitate the diffusion of nearby Li. To investigate this possibility, we performed AIMD at 600 K for 10 ps and measured how long Li⁺ stays close to a specific BH₄⁻ or PS₄³⁻ group once it has entered its environment. We define such an “interaction event” as occurring when Li⁺ comes within a distance that is set as the maximum of the first neighbor bond length observed in the density functional theory (DFT) relaxed structure, which is 2.2 Å for Li–H and 2.8 Å for Li–S. We have also tested our analysis with the Li–H cutoff distance being 2.8 Å while fixing the Li–S cutoff to be 2.8 Å. As indicated in Figure S₄, the conclusion that Li is less anchored by H still remains. Figure 4C shows the “escape curve” for both environments. More specifically, what is shown is the fraction of Li⁺ in an interaction event (y-axis) that has left again after a certain time (x-axis). It is clear that Li⁺ leaves the BH₄ environment very quickly (black curve in Figure 4C) as compared to the PS₄ environment, where the Li⁺ residence time is much longer (blue curves). A similar comparison is made between the Li–BH₄ residence time in Li₆PS₅BH₄ and the Li–Cl residence time in Li₆PS₅Cl in

Figure 4D. For $\text{Li}_6\text{PS}_5\text{Cl}$, the interact event radius was set as the maximum bond length of $\text{Li}-\text{Cl}$ (2.8 Å).

As can be inferred from Figure 4C, Li^+ is much more strongly anchored near the PS_4^{3-} group than near the BH_4^- group. Almost all “interaction events” around BH_4^- last less than 0.1 ps, whereas more than 40% of the events associated with the PS_4 group last longer than 0.1 ps. Moreover, ~10% of the Li^+ entering the PS_4 environment persist for longer than 1 ps, which is one-order-of-magnitude longer than the longest period of events around BH_4^- . It is also worth mentioning that such event duration of ~0.1–1 ps is roughly the same time scale of Li hopping, as observed in the Li hopping analysis in Figure S5.

Since the PS_4 group has a larger negative charge than BH_4^- one may suspect that electrostatics plays a dominant role in the anchoring of Li near PS_4 . But this is inconsistent with the data in Figure 4D which shows that even though $\text{Li}-\text{Cl}$ “interaction events” in $\text{Li}_6\text{PS}_5\text{Cl}$ have short residence times (more than 90% of the lithium escapes from the Cl^- environment occur in less than 0.25 ps), they are still substantially longer than the $\text{Li}-\text{BH}_4^-$ residence times, consistent with the increased ionic conductivity of BH_4^- -substituted argyrodite relative to that of $\text{Li}_6\text{PS}_5\text{Cl}$. It is also worth clarifying that the size of the BH_4^- cluster ion is similar to that of Cl^- because the $\text{Li}-\text{B}$ bond lengths in $\text{Li}_6\text{PS}_5\text{BH}_4^-$ are similar to the $\text{Li}-\text{Cl}$ bond lengths in $\text{Li}_6\text{PS}_5\text{Cl}$ (both range between 2.5 and 2.7 Å). Therefore, the enhancement of conductivity does not originate from the size difference between BH_4^- and Cl^- .

Our ab-initio analysis clearly indicates that BH_4^- anchors the Li ions much less than PS_4^{3-} or Cl^- in argyrodites. This weakened anchoring effect and consequently higher conductivity can have two possible origins: (1) a potential dynamic coupling between Li

diffusion and BH_4^- rigid rotation that facilitates Li conduction by lowering the activation barrier (also called the “Paddle-wheel” mechanism) and (2) a weaker interaction between Li-BH_4 that flattens the Li site energy landscape near BH_4^- , which facilitates the Li motion. Mechanism (1) has been frequently mentioned in recent papers as being responsible for fast Li conduction^{18,19,30,32}, whereas the role of mechanism (2) in contributing to the high conductivity has not been specifically evaluated. To determine whether both or one of these mechanisms contribute to the conductivity, we performed multiple analysis, as shown in Figure 5. In Figure 5A-D we quantify the dynamic correlation of Li diffusion and multiple motion degrees of freedoms in BH_4 unit, whereas in Figure 5E we quantify the local electronic interaction among Li-BH_4 , Li-PS_4 , and Li-Cl .

In principle, the BH_4 cluster ion has 15 degrees of freedom, as each of the atoms can displace in three dimensions. To facilitate the analysis of a possible dynamic correlation, two key modes of motion of BH_4 are considered: the stretching mode and the bending mode. The translational mode of BH_4 as a unit is not considered here since the motions that we investigate are relative to the B atom which is also the center of mass of BH_4 . The translational motion of BH_4 is captured in the motion of the Li atom relative to the B atom. As shown in Figure 5A, the first mode represents the stretching of the B–H bond, whereas the second mode reflects the bending of the B–H bond, which can lead to the rotation of H relative to B.

To quantify whether BH_4 rotates as a rigid body we investigate the correlation between the angular changes of the B-H bonds which should be pronounced if the BH_4 cluster rotates as a rigid body. However, our dynamic correlation analysis among the motion of the four B-H

bond angles shows very little correlation (Pearson correlation analysis at Supplemental Table 2 and Figure S8). Such observation indicates that the BH_4 unit does not rotate as a rigid body.

To quantify whether the Li motion is correlated with individual B-H bond motion, i.e., B-H bond stretching and B-H bond bending, the correlation between the B-H bond motion and Li position was calculated based on event analysis similar to the one used to generate Figure 4. We collect all the partial trajectories for which Li stays in a sphere within a cutoff distance of 3.0 \AA from the B atom as events to investigate possible correlation between Li motion and B-H bond motion. If the Li motion is correlated to B-H bond motion, it should show up in the Pearson correlation of trajectories. In atomic trajectories of 10 ps of AIMD simulation at 600 K, we tracked all the "events" for which Li is close enough to a BH_4 unit. For each of the "events", we obtain a time series of the Li-B and B-H displacement. We can then calculate and average the Pearson correlation coefficient of these two displacements with either stretching or bending. Both the histogram and estimated kernel density of the probability distribution of the average correlation of all the Li atoms are shown in Figure 5B.

For B-H bond stretching, we checked the correlation between changes in the B-H bond length and the Li-B distance. The Pearson coefficient⁴², in this case, is defined as:

$$\text{Corr} = \frac{\text{cov}(l_{\text{B-H}}(t), l_{\text{Li-B}}(t))}{\sigma(l_{\text{B-H}}(t))\sigma(l_{\text{Li-B}}(t))} \quad (1)$$

where $l_{\text{B-H}}(t)$ refers to the stretching length of the B-H bond, $l_{\text{Li-B}}(t)$ refers to the Li-B distance in the defined event, $\text{cov}(l_{\text{B-H}}(t), l_{\text{Li-B}}(t))$ refers to the covariance of Li-B distance and the stretching length of B-H bond while $\sigma(l_{\text{B-H}}(t))$ and $\sigma(l_{\text{Li-B}}(t))$ are the standard deviation of the Li-B distance and the stretching length of the B-H bond. For B-H bond bending, we evaluated the correlation between the B-H bending angle $\sigma(\theta_{\text{B-H}}(t))$ and the Li-B bending

angle $\sigma(\theta_{Li-B}(t))$. We use Li–B bending angle as an indication of the motion of Li with respect to the corresponding B–H bond because the displacement of the Li atom itself does not give the relative position information of Li with respect to the B–H bond. The intercorrelation between these two bending angles can then be quantified using the Pearson correlation coefficient:

$$Corr = \frac{cov(\theta_{B-H}(t), \theta_{Li-B}(t))}{\sigma(\theta_{B-H}(t))\sigma(\theta_{Li-B}(t))} \quad (2)$$

In equation (2), $cov(\theta_{B-H}(t), \theta_{Li-B}(t))$ refers to the covariance of two bending angles while $\sigma(\theta_{B-H}(t))$ and $\sigma(\theta_{Li-B}(t))$ are the standard deviation of the bending angles.

It can be clearly inferred from Figure 5B that neither the B–H bond stretching, nor the bond bending are particularly correlated to the motion of Li atoms nearby. The maximum correlation coefficient observed is less than 0.2, and most of the coefficients are smaller than 0.1. Given that a correlation smaller than 0.5 is generally regarded as weak correlation in statistics,^{43,44} the calculated value indicates that even though B–H bond bends and stretches very fast, the position of Li is not correlated to the movement of B–H bonds. Considering that rigid rotation of the BH_4 unit is absent, and the movement of in visual B–H bond shows little correlation with Li diffusion, there is no evidence to conclude that the enhanced conductivity in this material originates from a “paddle-wheel” mechanism.

To further corroborate the origin of weak correlation between BH_4 motion and Li diffusion, we calculated the frequencies of the stretching and bending degrees of freedom for the B–H bond, as shown in Figure 5C–D. For stretching degree of freedom, the frequency can be estimated as:

$$f_{stretching} = \frac{1}{l_{max}} \times \frac{d(l_{B-H})}{dt} \quad (3)$$

Here, l_{max} refers to the maximum amplitude of bond stretching as observed in the period of 10 ps. For bending degree of freedom, the frequency can be estimated as:

$$f_{bending} = \frac{1}{360^\circ} \times \frac{d(\theta_{B-H})}{dt}. \quad (4)$$

The evolution of frequencies of stretching and bending degrees of freedom are demonstrated in Figure 5C and Figure 5D. Since the frequency at each time frame is calculated from the first derivative of the velocities, the overall analysis will not significantly be modified by longer trajectories. We have also confirmed this by plotting the frequency evolution over the shorter time of 1 ps (Figure S6). As indicated in Figure 5C, the stretching frequency has a magnitude ranging from a few tens of THz to 200 THz, while the bending frequency in Figure 5D has a magnitude of several THz, which is consistent with observations on BH_4 groups in $Mg(BH_4)_4$.⁴⁵ Given that the Li hopping frequency is calculated to be well below 1 THz (Figure S5), it turns out that both B–H bond stretching, and bond bending occur at a higher-frequency time frame than the Li hops, so that B-H bond motion and Li motion can be decoupled.

Finally, To verify whether the weaker anchoring effect of BH_4^- on Li^+ is related to weak electronic interaction between Li^+ and BH_4^- , we calculated the integrated crystal orbital Hamilton population (-ICOHP) to quantify the chemical bonding strength of $Li-BH_4$, $Li-PS_4$, and $Li-Cl$ (Figure 5E).^{46,47} As shown in Figure 5E, the -ICOHP value of the $Li-BH_4$ bond is much smaller than that of the $Li-PS_4$ bond or $Li-Cl$ bond, which reveals significantly weaker electronic interaction. Therefore, we confirmed that the enhanced ionic conductivity has little to do with dynamic correlation among Li diffusion and B-H bond motion (e.g., the “paddle-wheel” mechanism) but is mostly caused by weak electronic interaction between the Li^+ and BH_4^- group. It should also be noted that the influence of weak electronic interaction between

Li and the anion framework on Li ionic conduction has also been discussed in the context of the inductive effect that central ions in MS_4 tetrahedra have on the Li conduction in LGPS-like structures.⁴⁸

4. CONCLUSION

In this work, we investigated the Li argyrodite system to explore the possibility of enhancing ionic conductivity through pseudohalogen substitution. Ab-initio computational screening to predict the synthetic accessibility of Li argyrodites with different pseudohalogen substitution suggested that among many possible polyanions, BH_4 could most likely substitute for the S on 4a and 4c sites in the argyrodite structure. This BH_4 -substituted Li argyrodites ($Li_{5.91}PS_{4.91}(BH_4)_{1.09}$) was successfully synthesized via a mechanochemical method and shows an ionic conductivity of 4.8 mS/cm, ~5-times higher than that of common halogen-substituted Li argyrodites (Li_6PS_5Cl and Li_6PS_5Br), confirming the positive contribution of a cluster ion to the Li-ion conductivity. AIMD analysis demonstrates that the enhancement of the Li-ion conductivity originates from the weaker anchoring effect the pseudohalide anion has on Li^+ . We found no evidence for any correlation between B-H bond motion and Li motion, indicating that no “paddle-wheel” effect is needed to explain the enhanced conductivity.

EXPERIMENTAL PROCEDURES

Resource Availability

Lead Contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Gerbrand Ceder (gceder@berkeley.edu).

Materials Availability

The materials generated in this study are available from the lead contact upon request.

Data and Code Availability

The authors declare that the data supporting the findings of this study are available within the paper and its supplemental information file. The data and code are available from the lead contact upon reasonable request.

Synthesis

β -Li₃PS₄ was synthesized using lithium sulfide (Li₂S, Sigma-Aldrich, 99.98% trace metals basis) and phosphor sulfide (P₂S₅, Sigma-Aldrich, 99%) mixed in a 2:1 molar ratio (excess P₂S₅ was used) in acetonitrile (Sigma-Aldrich, anhydrous, 99.8%). The suspension was stirred for 24 h and filtered to obtain the precipitate. The precipitate was washed with acetonitrile (ACN) 3 times and dried at 80 °C for 12 h to obtain Li₃PS₄·2ACN. The as-obtained Li₃PS₄·2ACN was then heated under vacuum at 150 °C for 24 h to obtain β -Li₃PS₄. The as-

synthesized β - Li_3PS_4 and LiBH_4 (Aldrich, >95%) were mixed in a 1:2 molar ratio and hand ground in an agate mortar for 15 min. Then, 0.8 g of the powder mixture and 80 g of zirconium oxide balls (5 mm in diameter) were placed into a zirconium oxide ball-mill jar and ball milled (SpexSamplePrep 8000M) for 2 h. To prevent the sample temperature from becoming too high, ball milling was paused for 15-min after every 30-min milling. The mixture was further annealed at 150 °C for 48 h to obtain BH_4 -substituted argyrodite. Because of the sensitivity to O_2 and moisture for the system, all the experimental procedures were performed in an argon atmosphere with <0.1 ppm of O_2 and H_2O .

$\text{Li}_6\text{PS}_5\text{X}$ (X = Cl, Br) samples were synthesized via a previously reported method.³ Lithium sulfide (Li_2S , Sigma-Aldrich, 99.98% trace metals basis), phosphor sulfide (P_2S_5 , Sigma-Aldrich, 99%), LiCl (Sigma-Aldrich, >99.98% trace metals basis), and LiBr (Sigma-Aldrich, >99%) were mixed in the appropriate stoichiometric ratio. The mixtures were hand ground in an agate mortar for 15 min and then pressed into pellets of 6.0 mm in diameter under a pressure of 2.0 metric tons for 4 min. The pellets were then filled into quartz ampules (12-mm inner diameter and ~15 cm in length), which were sealed under vacuum. The ampules were carbon-coated and preheated to avoid traces of water. The reaction was performed at 550 °C for 144 h to obtain $\text{Li}_6\text{PS}_5\text{X}$ (X = Cl, Br).

Cl-substituted argyrodite and Br-substituted argyrodite were also prepared by the same synthesis approach as was used for the BH_4 -substituted argyrodite. β - Li_3PS_4 and LiX (X = Cl, Br) were mixed in a 1:2 molar ratio and hand ground in an agate mortar for 15 min. Then, 0.8 g of the powder mixture and 80 g of zirconium oxide balls (5 mm in diameter) were placed into a zirconium oxide ball-mill jar and ball milled (SpexSamplePrep 8000M) for 2 h. Ball milling was

paused for 15-min after every 30-min milling. The mixture was further annealed at 150 °C for 48 h to obtain Cl-substituted argyrodite and Br-substituted argyrodite. The EIS of these halide-substituted argyrodites are shown in Figure S7.

Electrochemistry

The Li-ion conductivity was evaluated using EIS with tantalum metal as blocking electrodes at temperatures ranging from 20 °C to 85 °C. The solid-electrolyte powder was uniaxially compressed under a pressure of 520 MPa to make a ~1-mm-thick pellet with a diameter of 7.7 mm and then sandwiched by two tantalum foils. EIS measurements were performed using an EC-Lab Electrochemistry SP300 system (Biologic). The measurements were conducted at the initial open-circuit voltage in the frequency range of 7 MHz to 10 mHz with the application of a 10-mV signal amplitude. The measurements were performed using a Biologic controlled environment sample holder assembled and sealed in an Ar-filled glove box.

Solid-state cells were also fabricated in an Ar-filled glovebox. The cathode composite was prepared by first hand-mixing 65 mg of LBO-coated $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ powder (from Samsung Research Japan⁴⁰) and 30 mg of $\text{Li}_{5.91}\text{PS}_{4.91}(\text{BH}_4)_{1.09}$ for 20 min and then mixing them for another 20 min after adding 5 mg of carbon nano-fibers (CNFs, from Samsung Research Japan). The cell was assembled using a custom-made pressure cell consisting of a polyether ketone (PEEK) cylinder with an inner diameter of 8 mm and two 8-mm-diameter stainless-steel rods as current collectors. One end of the cylinder was first closed with a current collector. Then, 40 mg $\text{Li}_{5.91}\text{PS}_{4.91}(\text{BH}_4)_{1.09}$ as the electrolyte was added and compressed under a pressure of 100 MPa. Then, 5 mg of the cathode composite was spread evenly on top of the electrolyte

membrane and compacted under pressure of 200 MPa. Finally, an 8-mm-diameter piece of In metal was attached on the other side of the electrolyte membrane as the anode and compacted under 200-MPa pressure again. The entire cell was sealed in an Ar-filled jar and cycled under 5-MPa stack pressure provided by a spring. Cell cycling was performed using a Bio-Logic VMP300 system.

Characterization

For structure determination, synchrotron XRD data were collected at beamline 11BM at the Advanced Photon Source at Argonne National Laboratory. Because of the air sensitivity of the sample, the $\text{Li}_{5.91}\text{PS}_{4.91}(\text{BH}_4)_{1.09}$ powder was sealed into 0.0395-inch-diameter polyimide tubing in an argon glove box. Rietveld refinement was performed using the TOPAS V6 software package (Bruker). Chebyshev polynomials are used for the background fitting. Fundamental parameters approach is used for the peak shape modeling. The constrains for the structural factor refinement are as follows:

Occ(X) represents the site occupancy of atom X at related Wyckoff position.

(1) 4a sites are fully occupied by B1 and S1:

$$\text{Occ}(\text{B1}) + \text{Occ}(\text{S1}) = 1$$

(2) 4c sites are fully occupied by B2 and S2:

$$\text{Occ}(\text{B2}) + \text{Occ}(\text{S2}) = 1$$

(3) H1 is bonded to B1 and H2 is bonded to B2:

$$\text{Occ}(\text{B1}) = \text{Occ}(\text{H1}), \text{Occ}(\text{B2}) = \text{Occ}(\text{H2})$$

(4) Based on the charge balance, we could get:

$$12\text{Occ}(\text{Li}_1) + 6\text{Occ}(\text{Li}_2) + \text{Occ}(\text{B}_1) + \text{Occ}(\text{B}_2) = 7.$$

TEM ED and EDS measurements were performed on a FEI TitanX 60-300 microscope equipped with the Bruker windowless EDS detector at an accelerating voltage of 300 KV in the Molecular Foundry at LBNL. The simulated electron diffraction ring pattern for argyrodite structure (ICDD 04-018-1429) was generated with the Single Crystal 4 diffraction simulation software. Raman spectroscopy measurements were carried out using a home-built confocal micro-spectroscopy setup. Briefly, a Coherent Verdi-V2 single frequency laser was used as the excitation source at a wavelength of 532nm. The excitation laser was focused onto the sample surface using a 60X NA0.7 Nikon ELWD objective. The same objective collected the backscattered light. The collected signals were sent through 532nm notch filters to remove the Rayleigh line and then focused onto the entrance slit of a spectrometer. An IsoPlane 320 spectrometer equipped with an 1800 g/mm grating was used to disperse the signal onto a PIXIS 400 thermoelectrically cooled CCD. All samples were pellets pressed in an argon-filled glovebox and sealed using PET/PE encapsulations.

Computational methods

DFT Structural Optimization and Total Energy Calculations

Because of the partial occupancy of Li sites in the argyrodite structure, structural enumerations in a supercell with only 48h Li sites were performed, and first-principle calculations were performed on the top 10 structures with lowest electrostatic energy using DFT as implemented in the plane-wave-basis-set Vienna ab initio simulation package (VASP).

The structure with lowest DFT energy is then selected for further AIMD simulation. Projector augmented wave potentials with a kinetic energy cutoff of 520 eV were used in all the structural optimizations and total-energy calculations, and the exchange and correlation functionals were described within the Perdew–Burke–Ernzerhof generalized gradient approximation (GGA-PBE). The k-point grid in each dimension was set as 25 Å divided by the exact length of that dimension.

Phase Stability Analysis

The thermodynamic stability was evaluated using the calculated DFT total energy. The stability of any phase was evaluated by comparing its energy to linear combinations of the energy of other phases (leading to the same composition) using the convex-hull construction. The stability analysis was performed versus all the compounds in our internal database, which includes both phases from the Inorganic Crystal Structure Database (ICSD) [Inorganic Crystal Structure Database; <http://icsd.fiz-karlsruhe.de/icsd/>] and some compounds generated from data-mined substitution rules.⁴⁹ The phase stability was quantified by evaluating the energy above the hull (ehull), which refers to the compound decomposition energy to materials at the hull. A non-negative value of the ehull energy indicates a thermodynamic driving force for decomposition into alternate phases. To correct the overestimation of the binding energy by the GGA-PBE functional, we followed previous approaches^{50,51} to apply constant energy corrections of –0.66 eV per S atom. On the basis of the DFT calculated charge density and wavefunction, we performed COHP analysis using the LOBSTER package.^{46,47}

Li-Ion Diffusivity and Conductivity Calculations

AIMD simulation was used to investigate the ionic conductivity of Li ions. For all the

AIMD calculations, an NVT ensemble was applied with a time step of 1 fs and a Nosé–Hoover thermostat⁵² with a period of 100 fs. A minimal Γ -point-only grid was used with spin-polarized calculations. The AIMD simulations were run at 600 K, 700 K, 800 K, and 1000 K. All the data were fitted assuming Arrhenius behavior to obtain the activation energy, diffusion pre-factor, and room-temperature diffusivity. The lowest-energy atomic configurations were used as the initial configuration of the AIMD simulations.

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AUTHOR CONTRIBUTIONS

Conceptualization, Y.S., B.O., and G.C.; Methodology, Y.S. and B.O.; Formal Analysis, Y.S., B.O., Y.W., Z.C. and V.L.; Investigation, Y.S., B.O., Y.Z., S.S and Y.G.; Resources, Y.Z., S.S., and Y.G.; Writing-Original Draft, Y.S., B.O., and G.C.; Writing-Review & Editing, Y.S., B.O. and G.C.; Funding Acquisition, Y.G. and G.C.; Supervision, G.C.

DECLARATION OF INTERESTS

The authors declare no competing interests.

REFERENCES

1. Motavalli, J. (2015). Technology: A solid future. *Nature* 526, S96–S97. DOI:10.1038/526S96a.
2. Ceder, G., Ong, S.P., and Wang, Y. (2018). Predictive modeling and design rules for solid electrolytes. *MRS Bull.* 43, 782–788. DOI:10.1557/mrs.2018.210.
3. Deiseroth, H.J., Kong, S.T., Eckert, H., Vannahme, J., Reiner, C., Zaiß, T., and Schlosser, M. (2008). Li₆PS₅X: A class of crystalline Li-rich solids with an unusually high Li⁺ mobility. *Angew. Chemie - Int. Ed.* 47, 755–758. DOI:10.1002/anie.200703900.
4. Adeli, P., Bazak, J.D., Park, K.H., Kochetkov, I., Huq, A., Goward, G.R., and Nazar, L.F. (2019). Boosting Solid-State Diffusivity and Conductivity in Lithium Superionic Argyrodites by Halide Substitution. *Angew. Chemie* 131, 8773–8778. DOI:10.1002/ANGE.201814222.
5. D. Richards, W., Yan Wang, J. Miara, L., Chul Kim, J., and Gerbrand Ceder (2016). Design of Li_{1+2x}Zn_{1-x}PS₄, a new lithium ion conductor. *Energy Environ. Sci.* 9, 3272–3278. DOI:10.1039/C6EE02094A.
6. Murugan, R., Thangadurai, V., and Weppner, W. (2007). Fast lithium ion conduction in garnet-type Li₇La₃Zr₂O₁₂. *Angew. Chemie - Int. Ed.* 46, 7778–7781. DOI:10.1002/anie.200701144.
7. Shou-Hang Bo, Yan Wang, and Gerbrand Ceder (2016). Structural and Na-ion conduction characteristics of Na₃PS_xSe_{4-x}. *J. Mater. Chem. A* 4, 9044–9053. DOI:10.1039/C6TA03027K.
8. Wang, Y., Richards, W.D., Ong, S.P., Miara, L.J., Kim, J.C., Mo, Y., and Ceder, G. (2015). Design principles for solid-state lithium superionic conductors. *Nat. Mater.* 2015 1410 14, 1026–1031. DOI:10.1038/nmat4369.
9. Xiao, Y., Jun, K., Wang, Y., Miara, L.J., Tu, Q., and Ceder, G. (2021). Lithium Oxide Superionic Conductors Inspired by Garnet and NASICON Structures. *Adv. Energy Mater.* 11, 2101437. DOI:10.1002/AENM.202101437.
10. Richards, W.D., Wang, Y., Miara, L.J., Kim, J.C., and Ceder, G. (2016). Design of Li_{1+2x}Zn_{1-x}PS₄, a new lithium ion conductor. *Energy Environ. Sci.* 9, 3272–3278. DOI:10.1039/C6EE02094A.
11. Liu, Y., Wang, S., Nolan, A.M., Ling, C., Mo, Y., Li, N., Liu, Y., Wang, S., Nolan, A.M., et al. (2020). Tailoring the Cation Lattice for Chloride Lithium-Ion Conductors. *Adv. Energy Mater.* 10, 2002356. DOI:10.1002/AENM.202002356.
12. Wang, R., Ping, W., Wang, C., Liu, Y., Gao, J., Dong, Q., Wang, X., Mo, Y., Hu, L., Wang, R., et al. (2020). Computation-Guided Synthesis of New Garnet-Type Solid-State Electrolytes via an Ultrafast Sintering Technique. *Adv. Mater.* 32, 2005059. DOI:10.1002/ADMA.202005059.
13. Canepa, P., Bo, S.H., Sai Gautam, G., Key, B., Richards, W.D., Shi, T., Tian, Y., Wang, Y., Li, J., and Ceder, G. (2017). High magnesium mobility in ternary spinel chalcogenides. *Nat. Commun.* 2017 81 8, 1–8. DOI:10.1038/s41467-017-01772-1.
14. Matsuo, M., and Orimo, S.I. (2011). Lithium Fast-Ionic Conduction in Complex Hydrides: Review and Prospects. *Adv. Energy Mater.* 1, 161–172. DOI:10.1002/AENM.201000012.
15. Unemoto, A., Wu, H., Udovic, T.J., Matsuo, M., Ikeshoji, T., and Orimo, S.I. (2016). Fast

- lithium-ionic conduction in a new complex hydride-sulphide crystalline phase. *Chem. Commun.* *52*, 564–566. DOI:10.1039/c5cc07793a.
16. Wang, F., Evans, H.A., Kim, K., Yin, L., Li, Y., Tsai, P.-C., Liu, J., Lapidus, S.H., Brown, C.M., Siegel, D.J., et al. (2020). Dynamics of Hydroxyl Anions Promotes Lithium Ion Conduction in Antiperovskite Li_2OHCl . *Chem. Mater.* *32*, 8481–8491. DOI:10.1021/ACS.CHEMMATER.oCo2602.
 17. Fang, H., and Jena, P. (2017). Li-rich antiperovskite superionic conductors based on cluster ions. *Proc. Natl. Acad. Sci.* *114*, 11046–11051. DOI:10.1073/PNAS.1704086114.
 18. Fang, H., and Jena, P. (2018). Sodium Superionic Conductors Based on Clusters. *ACS Appl. Mater. Interfaces* *11*, 963–972. DOI:10.1021/ACSAMI.8B19003.
 19. Sun, Y., Wang, Y., Liang, X., Xia, Y., Peng, L., Jia, H., Li, H., Bai, L., Feng, J., Jiang, H., et al. (2019). Rotational Cluster Anion Enabling Superionic Conductivity in Sodium-Rich Antiperovskite Na_3OBH_4 . *J. Am. Chem. Soc.* *141*, 5640–5644. DOI:10.1021/JACS.9B01746.
 20. Zhou, L., Assoud, A., Zhang, Q., Wu, X., and Nazar, L.F. (2019). New Family of Argyrodite Thioantimonate Lithium Superionic Conductors. *J. Am. Chem. Soc.* *141*, 19002–19013. DOI:10.1021/JACS.9B08357.
 21. Zhou, L., Minafra, N., Zeier, W.G., and Nazar, L.F. (2021). Innovative Approaches to Li-Argyrodite Solid Electrolytes for All-Solid-State Lithium Batteries. *Acc. Chem. Res.* *54*, 2717–2728. DOI:10.1021/ACS.ACCOUNTS.oCoo874.
 22. Zhou, L., Park, K.H., Sun, X., Lalère, F., Adermann, T., Hartmann, P., and Nazar, L.F. (2019). Solvent-Engineered Design of Argyrodite $\text{Li}_6\text{PS}_5\text{X}$ (X = Cl, Br, I) Solid Electrolytes with High Ionic Conductivity. *ACS Energy Lett.* *4*, 265–270. DOI:10.1021/acsenerylett.8bo1997.
 23. Kaup, K., Bishop, K., Assoud, A., Liu, J., and Nazar, L.F. (2021). Fast Ion-Conducting Thioboracite with a Perovskite Topology and Argyrodite-like Lithium Substructure. *J. Am. Chem. Soc.* *143*, 6952–6961. DOI:10.1021/JACS.1C00941.
 24. Ouyang, B., Wang, Y., Sun, Y., and Ceder, G. (2020). Computational Investigation of Halogen-Substituted Na Argyrodites as Solid-State Superionic Conductors. *Chem. Mater.* *32*, 1896–1903. DOI:10.1021/ACS.CHEMMATER.9B04541.
 25. De Klerk, N.J.J., Rosłoń, I., and Wagemaker, M. (2016). Diffusion Mechanism of Li Argyrodite Solid Electrolytes for Li-Ion Batteries and Prediction of Optimized Halogen Doping: The Effect of Li Vacancies, Halogens, and Halogen Disorder. *Chem. Mater.* *28*, 7955–7963. DOI:10.1021/acs.chemmater.6b03630.
 26. Kraft, M.A., Culver, S.P., Calderon, M., Böcher, F., Krauskopf, T., Senyshyn, A., Dietrich, C., Zevalkink, A., Janek, J., and Zeier, W.G. (2017). Influence of Lattice Polarizability on the Ionic Conductivity in the Lithium Superionic Argyrodites $\text{Li}_6\text{PS}_5\text{X}$ (X = Cl, Br, I). *J. Am. Chem. Soc.* *139*, 10909–10918. DOI:10.1021/jacs.7b06327.
 27. Patel, S. V., Banerjee, S., Liu, H., Wang, P., Chien, P.H., Feng, X., Liu, J., Ong, S.P., and Hu, Y.Y. (2021). Tunable Lithium-Ion Transport in Mixed-Halide Argyrodites $\text{Li}_6\text{-xPS}_5\text{-xClBr}_x$: An Unusual Compositional Space. *Chem. Mater.* *33*, 1435–1443. DOI:10.1021/ACS.CHEMMATER.oCo4650.
 28. Feng, X., Chien, P.H., Wang, Y., Patel, S., Wang, P., Liu, H., Immediato-Scuotto, M., and Hu, Y.Y. (2020). Enhanced ion conduction by enforcing structural disorder in Li-deficient

- argyrodites $\text{Li}_6\text{-xPS}_5\text{-xCl}_{1+x}$. *Energy Storage Mater.* *30*, 67–73. DOI:10.1016/J.ENSM.2020.04.042.
29. Wang, P., Liu, H., Patel, S., Feng, X., Chien, P.H., Wang, Y., and Hu, Y.Y. (2020). Fast Ion Conduction and Its Origin in $\text{Li}_6\text{-xPS}_5\text{-xBr}_{1+x}$. *Chem. Mater.* *32*, 3833–3840. DOI:10.1021/ACS.CHEMMATER.9B05331.
 30. Smith, J.G., and Siegel, D.J. (2020). Low-temperature paddlewheel effect in glassy solid electrolytes. *Nat. Commun.* *2020* *111* *11*, 1–11. DOI:10.1038/s41467-020-15245-5.
 31. Song, A.-Y., Turcheniuk, K., Leisen, J., Xiao, Y., Meda, L., Borodin, O., and Yushin, G. (2020). Understanding Li-Ion Dynamics in Lithium Hydroxychloride (Li_2OHCl) Solid State Electrolyte via Addressing the Role of Protons. *Adv. Energy Mater.* *10*, 1903480. DOI:10.1002/AENM.201903480.
 32. Zhang, Z., Roy, P.-N., Li, H., Avdeev, M., and Nazar, L.F. (2019). Coupled Cation–Anion Dynamics Enhances Cation Mobility in Room-Temperature Superionic Solid-State Electrolytes. *J. Am. Chem. Soc.* *141*, 19360–19372. DOI:10.1021/JACS.9B09343.
 33. Ong, S.P., Wang, L., Kang, B., and Ceder, G. (2008). Li–Fe–P–O₂ Phase Diagram from First Principles Calculations. *Chem. Mater.* *20*, 1798–1807. DOI:10.1021/CM702327G.
 34. Ong, S.P., Mo, Y., Richards, W.D., Miara, L., Lee, H.S., and Ceder, G. (2012). Phase stability, electrochemical stability and ionic conductivity of the $\text{Li}_{10\pm 1}\text{MP}_2\text{X}_{12}$ (M = Ge, Si, Sn, Al or P, and X = O, S or Se) family of superionic conductors. *Energy Environ. Sci.* *6*, 148–156. DOI:10.1039/C2EE23355J.
 35. Mo, Y., Ong, S.P., and Ceder, G. (2012). First principles study of the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ lithium super ionic conductor material. *Chem. Mater.* *24*, 15–17. DOI:10.1021/CM203303Y.
 36. Sun, W., Dacek, S.T., Ong, S.P., Hautier, G., Jain, A., Richards, W.D., Gamst, A.C., Persson, K.A., and Ceder, G. (2016). The thermodynamic scale of inorganic crystalline metastability. *Sci. Adv.* *2*, e1600225. DOI:10.1126/sciadv.1600225.
 37. Sakuda, A., Yamauchi, A., Yubuchi, S., Kitamura, N., Idemoto, Y., Hayashi, A., and Tatsumisago, M. (2018). Mechanochemically Prepared $\text{Li}_2\text{S-P}_2\text{S}_5\text{-LiBH}_4$ Solid Electrolytes with an Argyrodite Structure. *ACS Omega* *3*, 5453–5458. DOI:10.1021/ACSOMEGA.8B00377.
 38. Züttel, A., Wenger, P., Rentsch, S., Sudan, P., Mauron, P., and Emmenegger, C. (2003). LiBH_4 a new hydrogen storage material. *J. Power Sources* *118*, 1–7. DOI:10.1016/S0378-7753(03)00054-5.
 39. Wu, L., Zhang, Z., Liu, G., Weng, W., Zhang, Z., and Yao, X. (2021). Wet-Milling Synthesis of Superionic Lithium Argyrodite Electrolytes with Different Concentrations of Lithium Vacancy. *ACS Appl. Mater. Interfaces* *13*, 46644–46649. DOI:10.1021/ACSAMI.1C13031.
 40. Zhang, Y.-Q., Tian, Y., Xiao, Y., Miara, L.J., Aihara, Y., Tsujimura, T., Shi, T., Scott, M.C., and Ceder, G. (1903). Direct Visualization of the Interfacial Degradation of Cathode Coatings in Solid State Batteries: A Combined Experimental and Computational Study. DOI:10.1002/aenm.201903778.
 41. Tian, Y., Shi, T., Richards, W.D., Li, J., Kim, J.C., Bo, S.-H., and Ceder, G. (2017). Compatibility issues between electrodes and electrolytes in solid-state batteries. *Energy Environ. Sci.* *10*, 1150–1166. DOI:10.1039/C7EE00534B.

42. Soper, H.E., Young, A.W., Cave, B.M., Lee, A., and Pearson, K. (1917). On the Distribution of the Correlation Coefficient in Small Samples. Appendix II to the Papers of "Student" and R. A. Fisher. *Biometrika* *11*, 328. DOI:10.2307/2331830.
43. Rodgers, J.L., and Nicewander, ; W Alan (1988). Thirteen Ways to Look at the Correlation Coefficient. *Am. Stat.* *42*, 59–66.
44. Buda, A., and Jarynowski, A. (2010). Life time of correlations and its applications (Andrzej Buda Wydawnictwo Niezależne).
45. George, L., Drozd, V., Saxena, S.K., Bardaji, E.G., and Fichtner, M. (2009). Structural Phase Transitions of Mg(BH₄)₂ under Pressure. *J. Phys. Chem. C* *113*, 486–492. DOI:10.1021/JP807842T.
46. Dronskowski, R., and Blochl, P.E. (1993). Crystal Orbital Hamilton Populations (COHP). Energy-Resolved Visualization of Chemical Bonding in Solids Based on Density-Functional Calculations. *J. Phys. Chem* *97*, 8617–8624. DOI: 10.1021/J100135A014.
47. Deringer, V.L., Tchougréeff, A.L., and Dronskowski, R. (2011). Crystal Orbital Hamilton Population (COHP) Analysis As Projected from Plane-Wave Basis Sets. *J. Phys. Chem. A* *115*, 5461–5466. DOI:10.1021/JP202489S.
48. Culver, S.P., Squires, A.G., Minafra, N., Armstrong, C.W.F., Krauskopf, T., Böcher, F., Li, C., Morgan, B.J., and Zeier, W.G. (2020). Evidence for a Solid-Electrolyte Inductive Effect in the Superionic Conductor Li₁₀Ge_{1-x}Sn_xP₂S₁₂. *J. Am. Chem. Soc.* *142*, 21210–21219. DOI:10.1021/JACS.0C10735.
49. Hautier, G., Fischer, C., Ehrlacher, V., Jain, A., and Ceder, G. (2010). Data Mined Ionic Substitutions for the Discovery of New Compounds. *Inorg. Chem.* *50*, 656–663. DOI:10.1021/IC102031H.
50. Wang, L., Maxisch, T., and Ceder, G. (2006). Oxidation energies of transition metal oxides within the GGA+U framework. *Phys. Rev. B - Condens. Matter Mater. Phys.* *73*, 195107. DOI:10.1103/PhysRevB.73.195107.
51. Wang, Y., Richards, W.D., Bo, S.-H., Miara, L.J., and Ceder, G. (2017). Computational Prediction and Evaluation of Solid-State Sodium Superionic Conductors Na₇P₃X₁₁ (X = O, S, Se). *Chem. Mater.* *29*, 7475–7482. DOI:10.1021/ACS.CHEMMATER.7B02476.
52. Nosé, S. (1984). A unified formulation of the constant temperature molecular dynamics methods. *J. Chem. Phys.* *81*, 511–519. DOI:10.1063/1.447334.

FIGURE AND SCHEME TITLES AND LEGENDS

Figure 1. Structure and stability of Li argyrodites

- (A) General structure of argyrodite with different sulfur sites distinguished by colors (4a with red, 4c with green, and 16e with yellow).
(B) Sulfur site occupancy for four types of substitution.
(C) Energy above the hull (E_{hull}) of different substitutions.

Figure 2. Characterization of as-synthesized BH_4 -argyrodite

- (A) Synchrotron XRD pattern of as-synthesized BH_4 -argyrodite.
(B) Electron diffraction pattern of as-synthesized BH_4 -argyrodite. Calculated diffraction rings of the argyrodite structure are shown in the bottom right corner.
(C) STEM/EDS mapping of the element distribution in a representative particle cluster of the BH_4 -argyrodite (scale bar: 100 nm).
(D and E) Raman spectra of $\text{Li}_6\text{PS}_5\text{Cl}$, $\text{Li}_{5.91}\text{PS}_{4.91}(\text{BH}_4)_{1.09}$, LiBH_4 , $\beta\text{-Li}_3\text{PS}_4$, and PET/PE (background) in the 100 cm^{-1} to 500 cm^{-1} region and 2000 cm^{-1} to 2800 cm^{-1} region.

Figure 3. Electrochemical Performance of BH_4 -argyrodite

- (A) EIS plots of $\text{Li}_{5.91}\text{PS}_{4.91}(\text{BH}_4)_{1.09}$ (LPSBH, red points) and $\beta\text{-Li}_3\text{PS}_4$ (β -LPS, blue points) at RT.
(B) EIS plots of $\text{Li}_{5.91}\text{PS}_{4.91}(\text{BH}_4)_{1.09}$ at 25°C (blue circle), 40°C (green rhombus), 55°C (orange triangle), 70°C (purple square), and 85°C (red star).
(C) Arrhenius plot of $\text{Li}_{5.91}\text{PS}_{4.91}(\text{BH}_4)_{1.09}$ (red triangle), $\text{Li}_6\text{PS}_5\text{Cl}$ (blue sphere), and $\text{Li}_6\text{PS}_5\text{Br}$ (yellow rhombus).
(D) Electrochemical charge and discharge of (+) $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ | $\text{Li}_{5.91}\text{PS}_{4.91}(\text{BH}_4)_{1.09}$ | In (-) all-solid-state battery between 1.4 and 3.7 V at a current density of 0.05 mA/cm^2 . The cell was held at 3.7 V for 3 hours after charging. See also Figure S3.

Figure 4. AIMD simulation of $\text{Li}_6\text{PS}_5\text{BH}_4$ and $\text{Li}_6\text{PS}_5\text{Cl}$

- (A) Trajectories of one selected Li atom with its neighboring BH_4 (B is buried within the spherical trajectory of H) polyanion.
(B) Trajectories of one selected Li atom with its neighboring PS_4 polyanion.
(C) Fraction of events occurring around BH_4 and PS_4 in $\text{Li}_6\text{PS}_5\text{BH}_4$ during a simulation time of 10 ps in 600 K (semilogarithmic plot in the set). See also Figure S4.
(D) Fraction of events occurring around BH_4 in $\text{Li}_6\text{PS}_5\text{BH}_4$ and Cl in $\text{Li}_6\text{PS}_5\text{Cl}$ during a simulation time of 10 ps in 600 K (semilogarithmic plot in the set). An event is defined as a Li atom entering a sphere of radius $r_{\text{Li-H}} = 2.2\text{ \AA}$, $r_{\text{Li-Cl}} = 2.8\text{ \AA}$ or $r_{\text{Li-S}} = 2.8\text{ \AA}$.

Figure 5. Correlation analysis between BH₄ and Li

(A) Demonstration of the relationship between B-H bond motion and Li diffusion. The motion of B-H bond can be decomposed into stretching and bending modes of the B-H bond.

(B) Probability distribution of the Pearson correlation between the stretching of the B-H bond and Li motion as well as the probability distribution of Pearson correlation between the bending of the B-H bond and Li motion.

(C) Demonstration of the calculated frequency evolution of the B-H bond stretching degree of freedom as a function of time for selected BH₄ unit as shown in (A).

(D) Demonstration of the calculated frequency evolution of the B-H bond bending degree of freedom as a function of time for selected BH₄ unit as shown in (A). See also Figure S6.

(E) Kernel density distribution of calculation -ICOHP value of Li-Cl, Li-BH₄, and Li-PS₄ bonding in Li₆PS₅Cl and Li₆PS₅BH₄.

TABLES AND TABLE TITLES AND LEGENDS

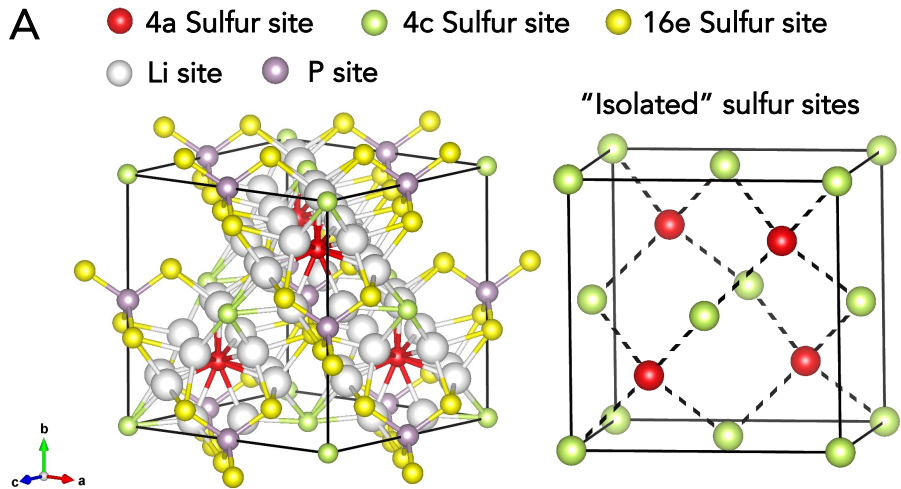
Table 1. Competing phases for BH₄ substitution and halide substitution.

Materials	Competing Phases	Materials	Competing Phases
Li ₆ PS ₅ BH ₄	LiSH + Li ₂ S + BP	Li ₆ PS ₅ X (X=Cl, Br, I)	Li ₃ PS ₄ + Li ₂ S + LiX
Li ₅ PS ₄ (BH ₄) ₂	LiBH ₄ + LiSH + BP	Li ₅ PS ₄ X ₂ (X=Cl, Br, I)	Li ₃ PS ₄ + Li ₂ S + LiX

Table 2. Atomic site information for BH₄-substituted Li argyrodite based on Rietveld refinement of synchrotron XRD data

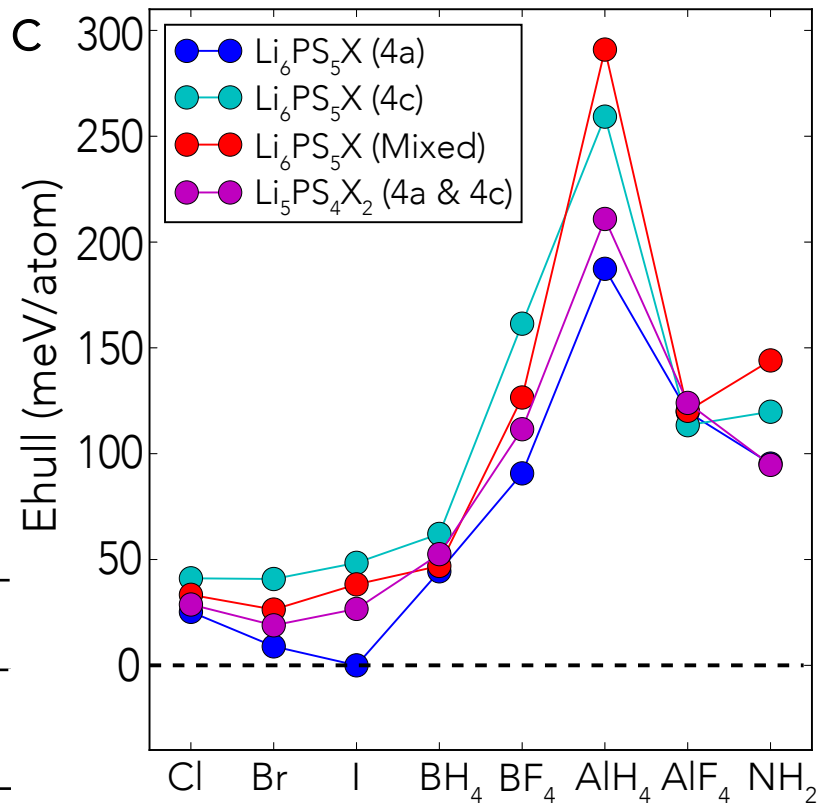
Atom	Wyckoff position	x	y	z	B _{iso} / Å ²	Site occupancy
Li1	48h	0.3053(2)	0.3053(2)	0.0024(8)	4	0.334(4)
Li2	24g	0.75	0.0386(4)	0.25	4	0.315(9)
B1	4a	0	0	0	4.2(4)	0.584(8)
S1	4a	0	0	0	4.2(4)	0.416(8)
B2	4c	0.25	0.25	0.25	4.2(4)	0.506(7)
S2	4c	0.25	0.25	0.25	4.2(4)	0.494(7)
P1	4b	0.5	0.5	0.5	3.6(6)	1
S3	16e	0.6200(7)	0.6200(7)	0.6200(7)	3.6(6)	1
H1	16e	0.0761(1)	0.0761(1)	-0.0761(1)	1	0.584(8)
H2	16e	0.1739(1)	0.1739(1)	0.1739(1)	1	0.506(7)

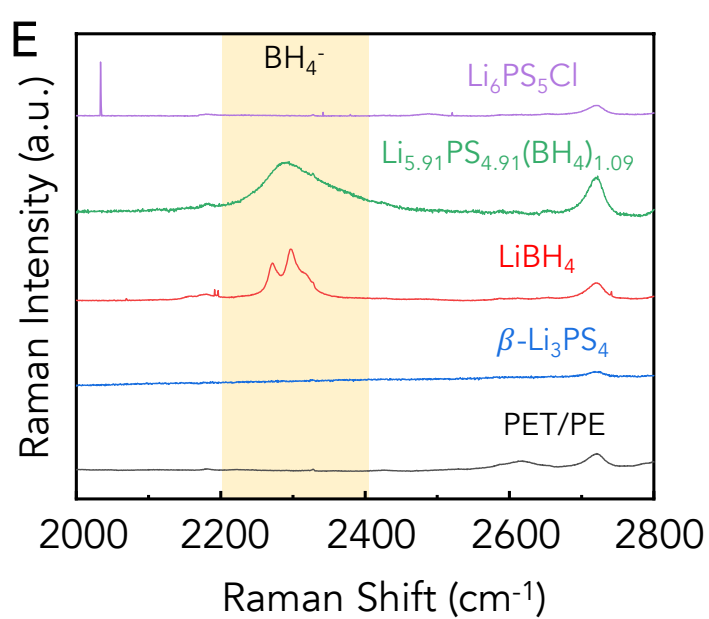
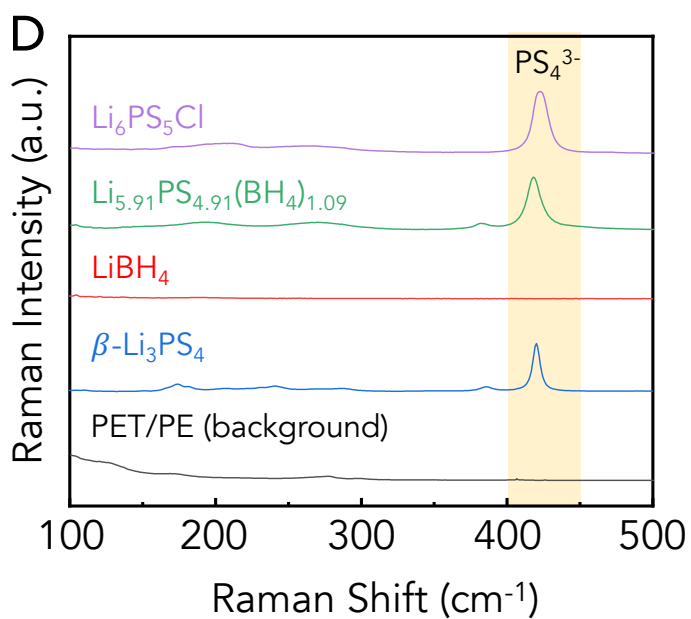
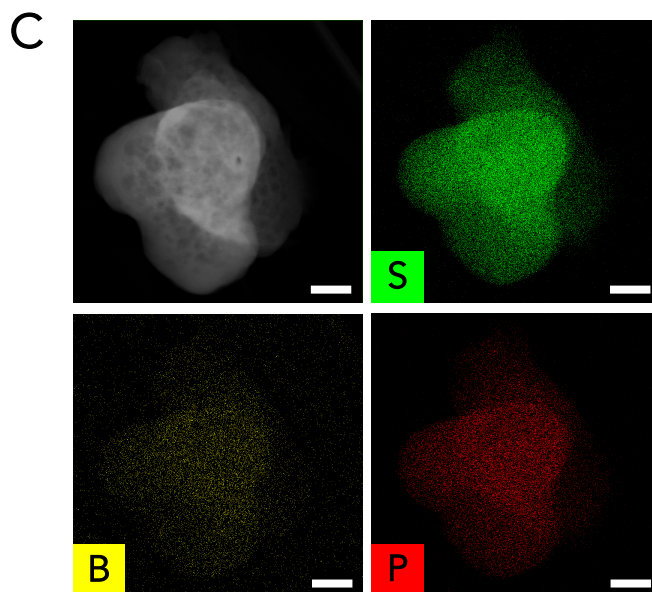
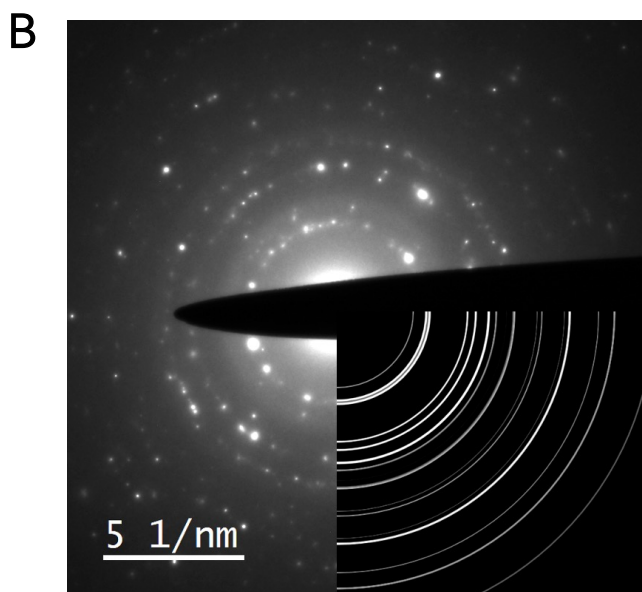
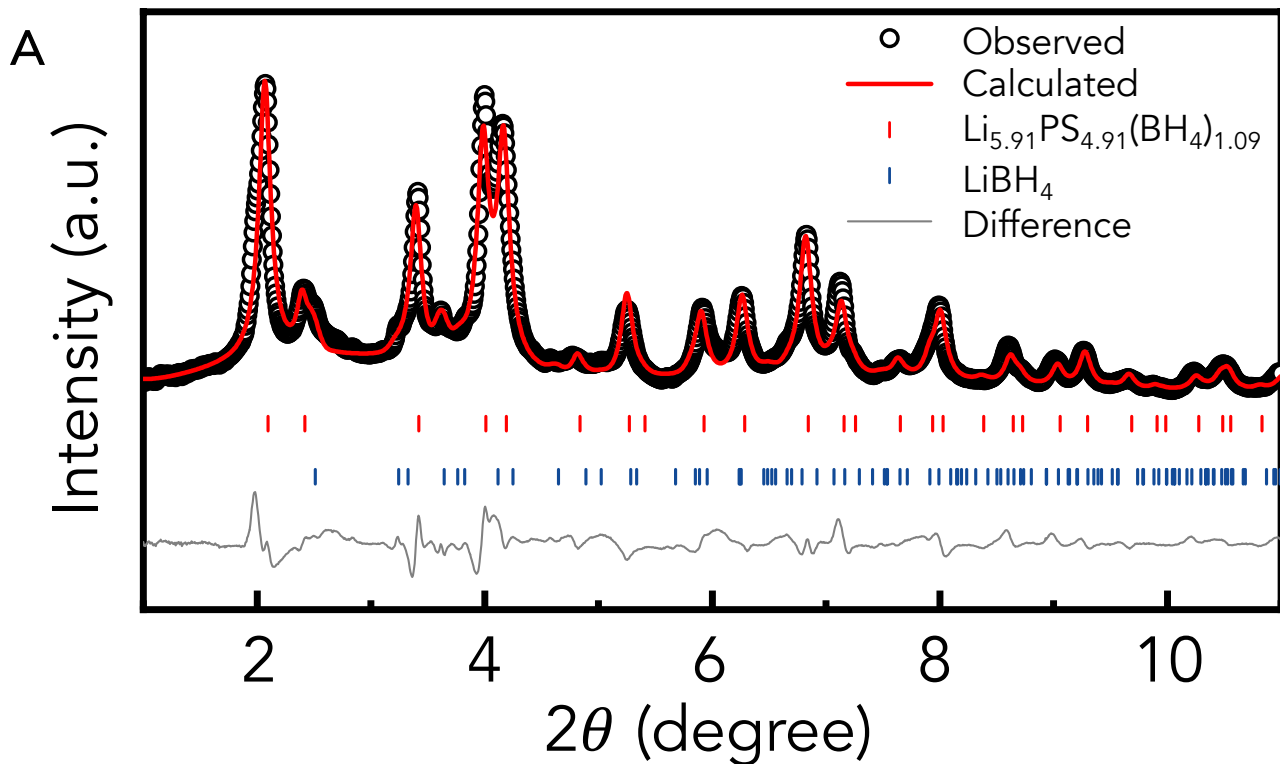
Space group: F-43m, Lattice parameter: a = 10.0112(7) Å, R-factor: Rwp = 7.63%

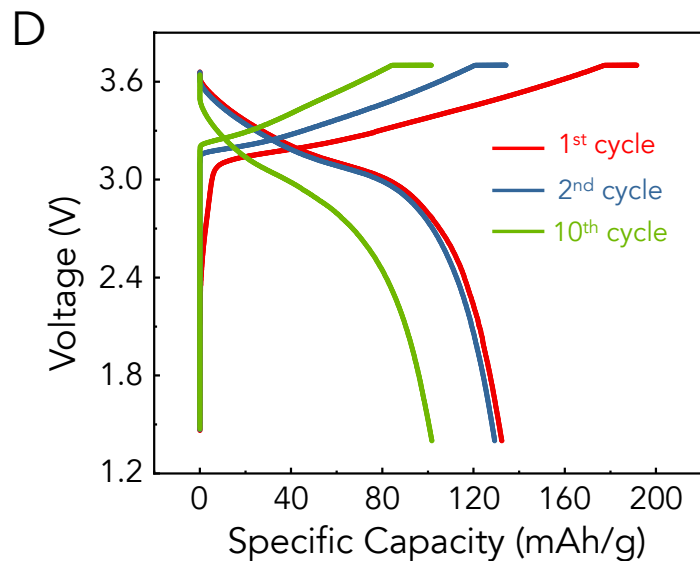
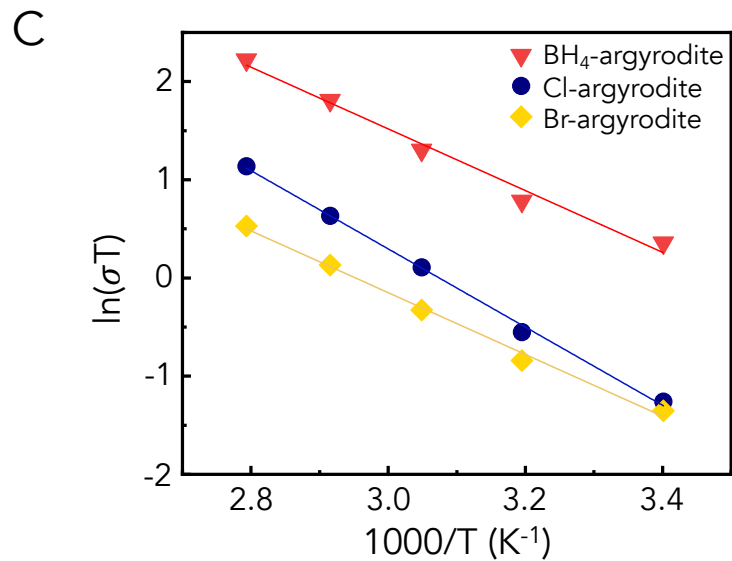
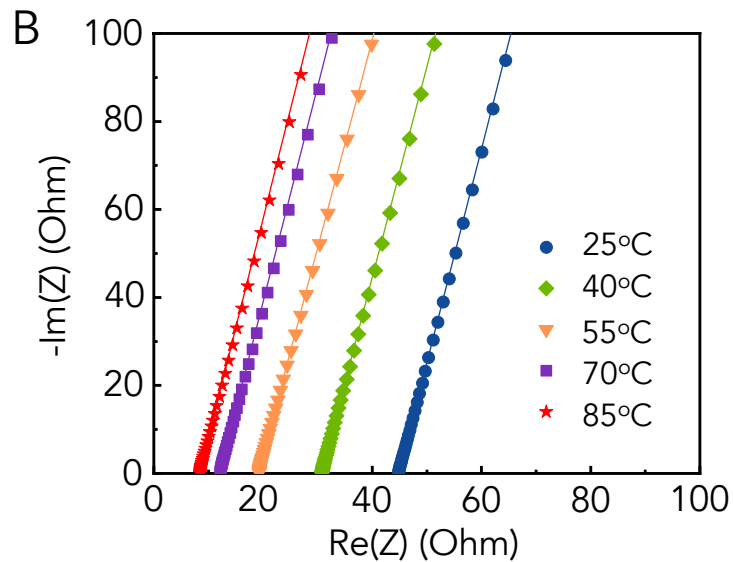
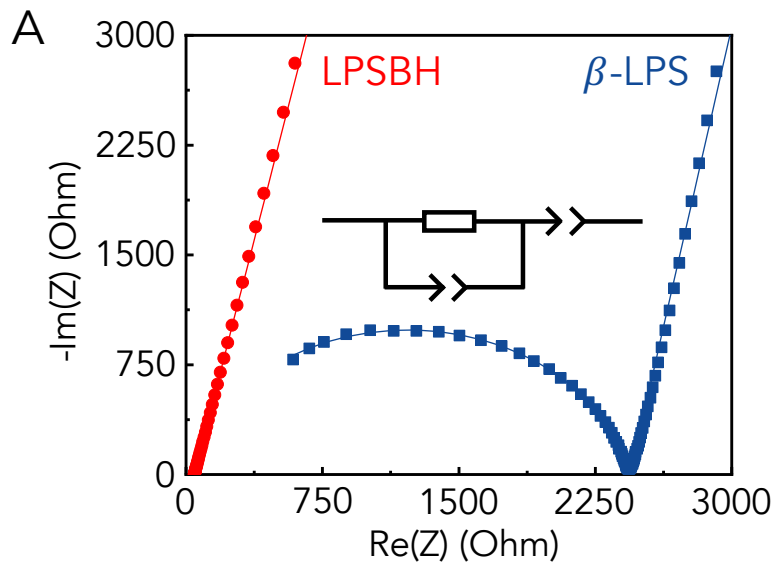


B

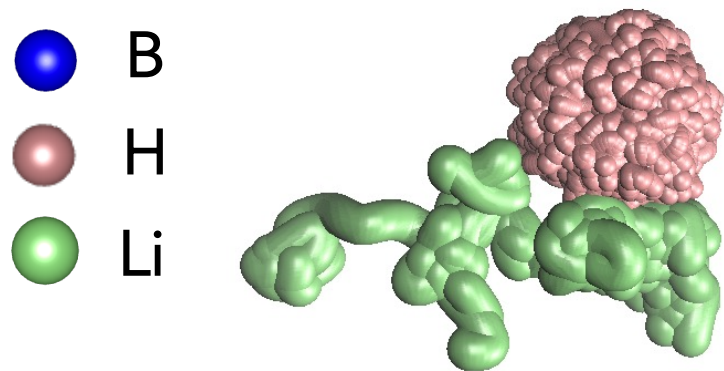
Configuration	$\text{Li}_6\text{PS}_5\text{X}$ (4a)	$\text{Li}_6\text{PS}_5\text{X}$ (4c)	$\text{Li}_5\text{PS}_4\text{X}$ (Mixed)	$\text{Li}_6\text{PS}_5\text{X}_2$ (4a & 4c)
4a Site	1.0	0.0	0.5	1.0
4c Site	0.0	1.0	0.5	1.0



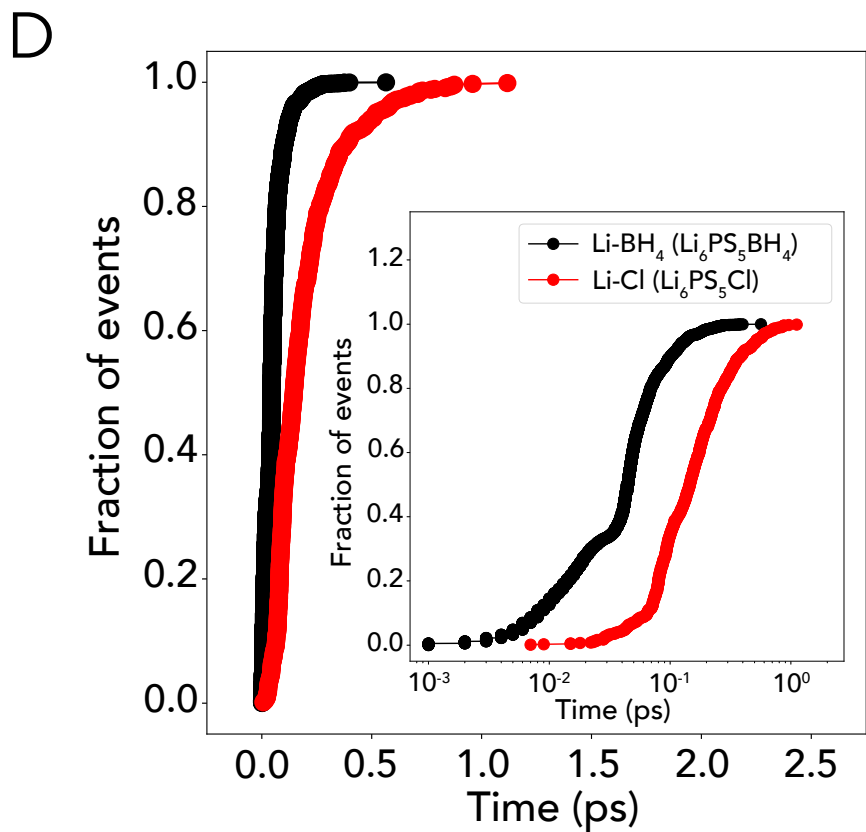
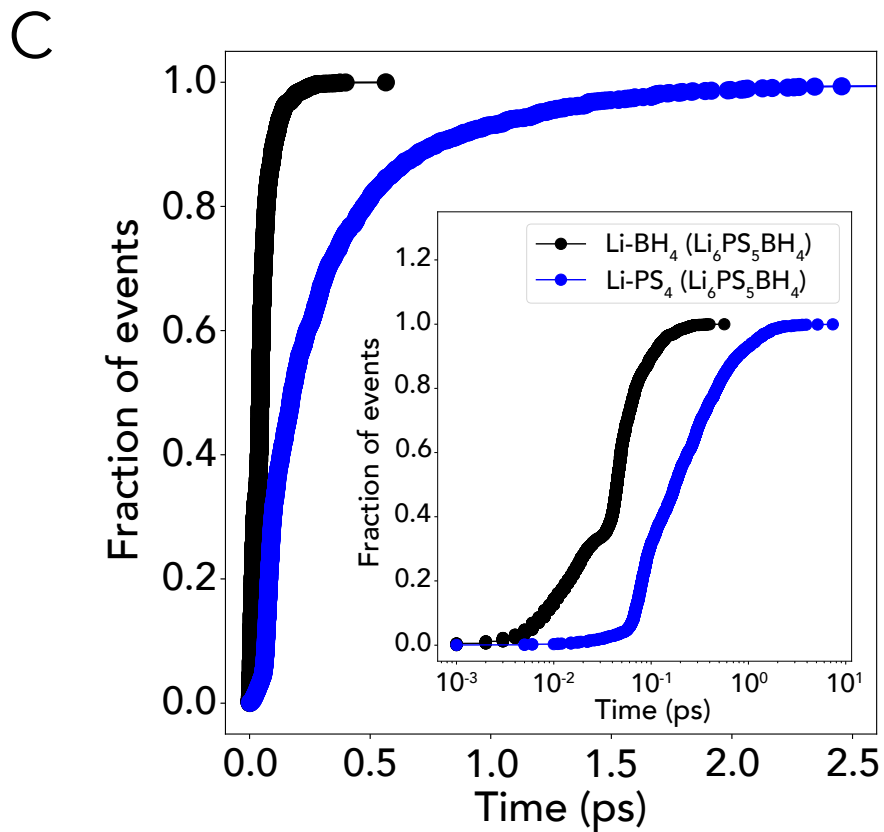
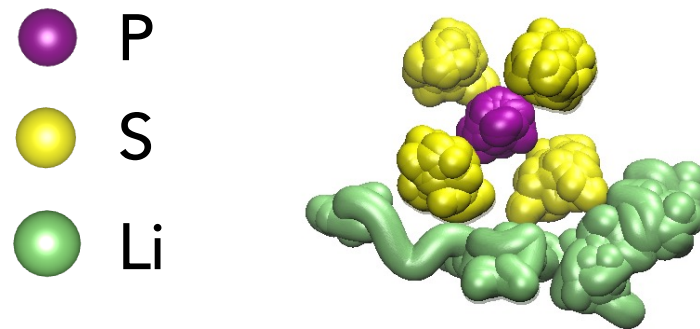


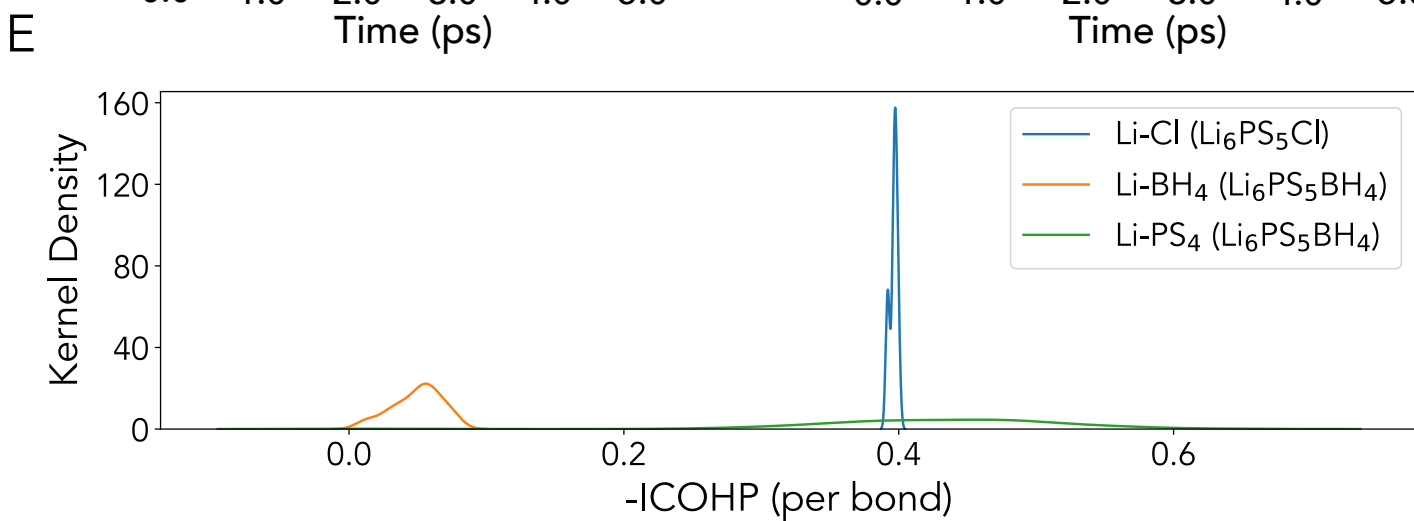
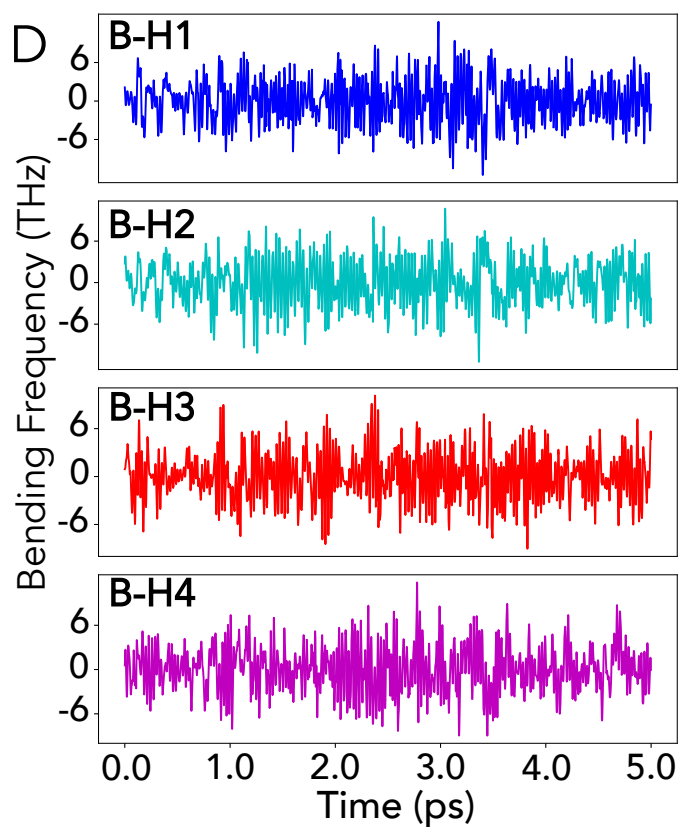
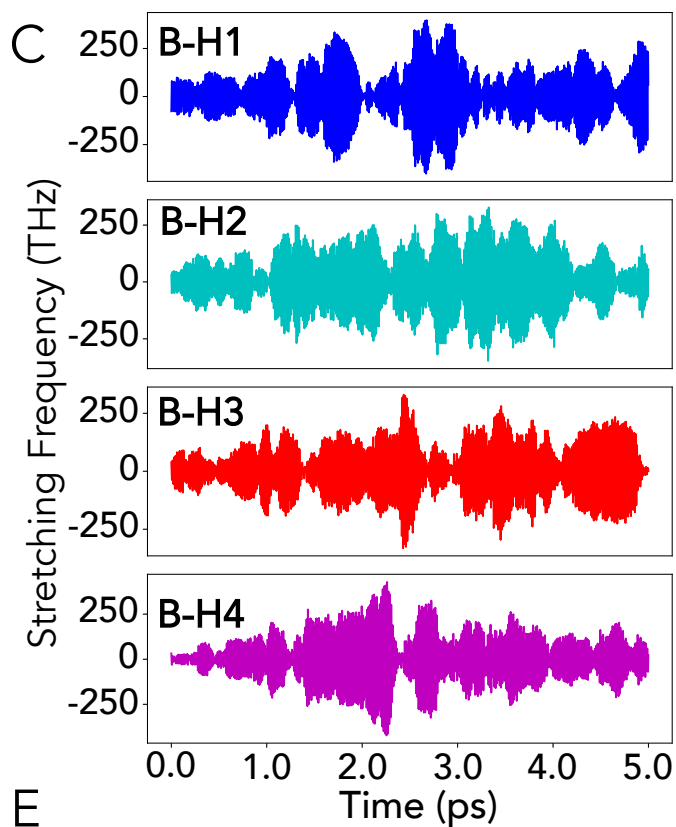
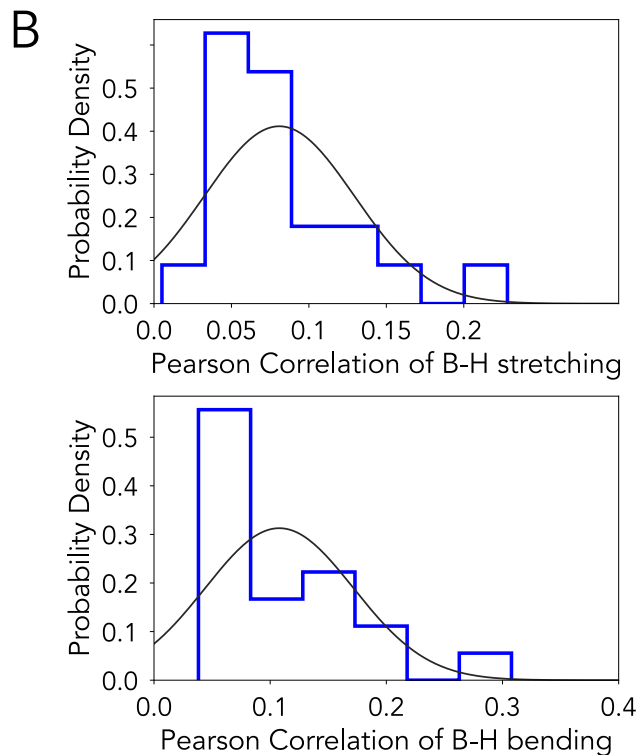
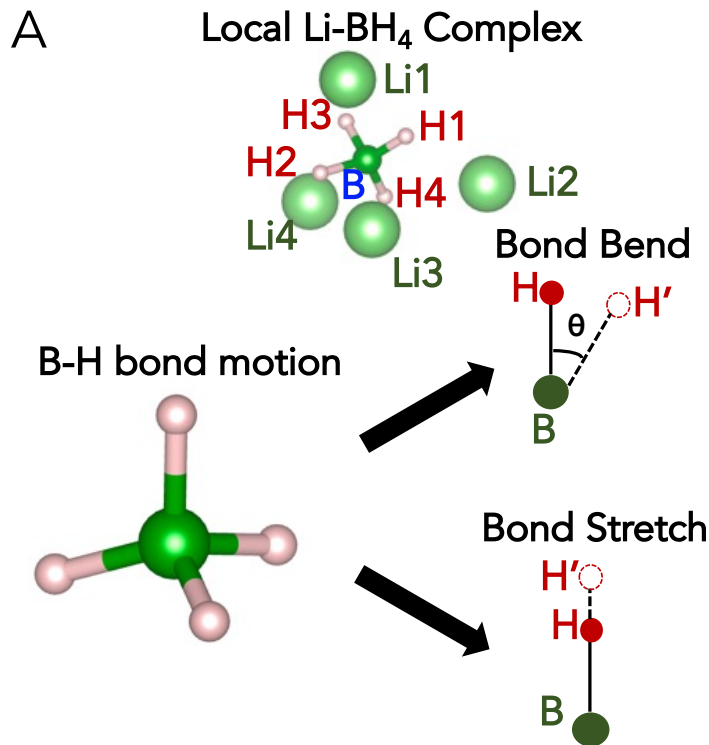


A Trajectory of Li motion and nearest BH_4 in 10 ps

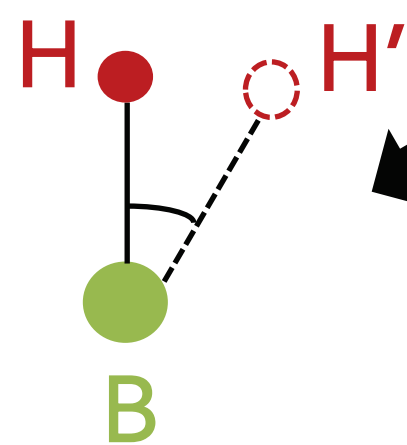
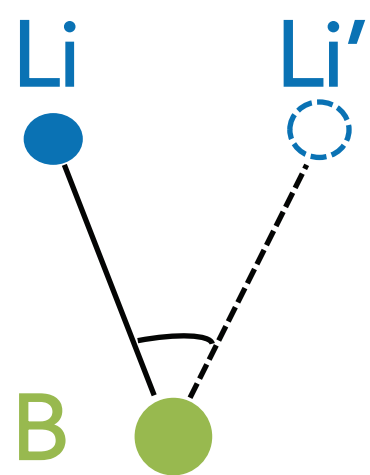


B Trajectory of Li motion and nearest PS_4 in 10 ps

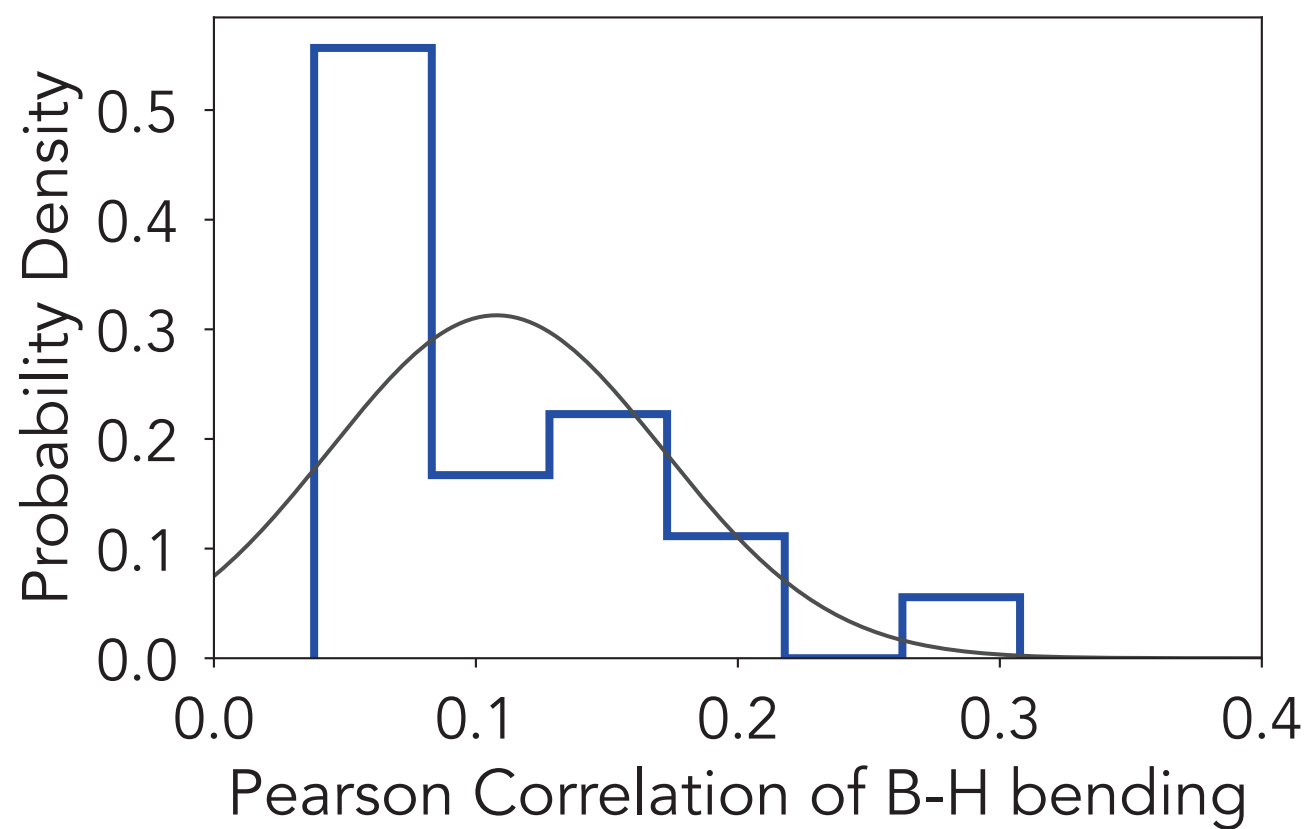




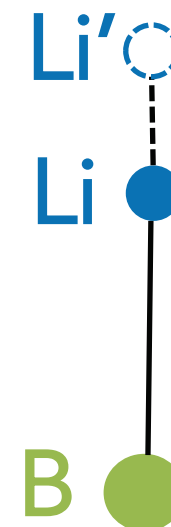
Angular Li motion



B-H Bond Bend



Radial Li motion



B-H Bond Stretch

