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Tuning mobility and stability of lithium ion conductors based on lattice dynamics†

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Lithium ion conductivity in many structural families can be tuned by many orders of magnitude, with some rivaling that of liquid electrolytes at room temperature. Unfortunately, fast lithium conductors exhibit poor stability against lithium battery electrodes. In this article, we report a fundamentally new approach to alter ion mobility and stability against oxidation of lithium ion conductors using lattice dynamics. By combining inelastic neutron scattering measurements with density functional theory, fast lithium conductors were shown to have low lithium vibration frequency or low center of lithium phonon density of states. On the other hand, lowering anion phonon densities of states reduces the stability against electrochemical oxidation. Olivines with low lithium band centers but high anion band centers are promising lithium ion conductors with high ion conductivity and stability. Such findings highlight new strategies in controlling lattice dynamics to discover new lithium ion conductors with enhanced conductivity and stability.

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Broader context

Replacing organic liquid electrolytes with solid lithium ion conductors in Li-ion batteries can boost the energy density and also increase battery safety. Current research and development of solid-state lithium ion batteries has been catalyzed by recent breakthroughs in solid lithium ion conductors that have ion conductivities rivaling those of conventional organic liquid electrolytes. However, known fast solid lithium ion conductors are not stable against lithium ion battery electrodes. Of significance, no fast lithium ion conductor known to date is stable against positive electrode materials in lithium ion batteries. Therefore, it is of great importance to design new lithium ion conductors having not only high Li conductivity but also being stable during battery operation. Increasing ion mobility and stability of lithium solid conductors is not straightforward and progress in the past decades has been achieved primarily by trial and error. Structural and chemical tuning *via* isovalent or aliovalent substitution of cation and/or anion in given structural families has led to steady increase in the lithium ion conductivity, and recent discovery of superionic lithium ion conductors. In this article, we report correlations between lattice dynamics and ion mobility or stability against electrochemical oxidation, and highlight opportunities to search for fast, stable lithium ion conductors based on low lithium band center but high anion band center. With rapid advances in the computational capability, we envision these descriptors to be used in high-throughput studies to screen not only lithium ion conductors but also other technologically relevant ion conductors such as oxygen or sodium ion conductors.

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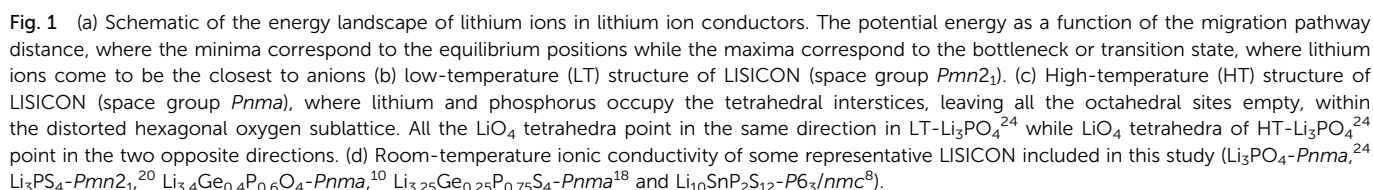
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Introduction

Replacing organic liquid electrolytes^{1,2} with solid lithium ion conductors in lithium ion batteries enables the use of the metallic lithium to markedly boost the energy density^{3,4} and also increases battery safety.⁵ Current research and development of solid-state lithium ion batteries has been catalyzed by recent breakthroughs in solid lithium ion conductors that have ion conductivities^{6–9} rivaling that of conventional organic liquid electrolytes.¹ Although a number of structural families such as lithium superionic conductors (LISICON),^{10,11} garnets,¹² NASICON-like (sodium superionic conductor),¹³ and perovskites¹⁴ have ion conductivities approaching that of liquid electrolytes, an increasing number of experimental¹⁵ and computational^{16,17}





Increasing ion mobility and stability of lithium solid conductors is not straightforward and progress in the past decades has been achieved primarily by trial and error. Structural and chemical tuning *via* isovalent or aliovalent substitution of cation^{10,11} and/or anion^{18–20} in given structural families has led to steady increase in the lithium ion conductivity, and recent discovery of superionic lithium ion conductors.^{6–9} Recently a number of structure-based ion conductivity descriptors have been proposed to aid and accelerate the design of new superionic conductors including the volume of the unit cell^{10,13,21} the volume of lithium diffusion pathway,²² the anion in the structure,²¹ and the structure of the anion sublattices.²³ For example, increasing lattice volume in the LISICON,¹⁰ NASICON-like,¹³ or perovskite^{14,21} structure can enhance ion conductivity and reduce activation energy.²¹ In addition, changing the anions by moving down in the periodic table (*e.g.* Li₁₀GeP₂X₁₂, (X = O, S and Se)¹⁷ or Li₃PX₄ (X = O²⁴ and S²⁰)) and/or arranging anions in a body centered cubic lattice²³ can increase lithium ion conductivity by reducing activation energy. Unfortunately, most of these descriptors have limited predictive power when applied across different structure families and chemistry of lithium ion conductors.²¹ Direct computation of Li-ion conductivity using *ab initio* molecular dynamics (AIMD) has also been pursued as a way to discover/design new materials with higher ionic conductivity.^{25,26} However, this method is computationally very demanding not to mention various practical limitations such as the need to extrapolate ionic conductivity from high temperature to room temperature. Moreover, no design principle is established

for the stability of lithium solid conductors. Limited predictive power of reported conductivity descriptors and the lack of stability descriptor hampers the search for new lithium-ion conductors with enhanced conductivity and stability in order to meet all the requirements of solid-state lithium-ion batteries. In this article, we report a new approach to design lithium ion mobility and stability of lithium ion conductors using their lattice dynamical properties. We relate lithium ion mobility to lattice dynamics based on the following hypothesis: small energetic barrier for lithium ion migration (enthalpy of migration) is associated with large displacement amplitude from their equilibrium sites (Fig. 1a), rendering greater probability for lithium ions to explore multiple energy minima. Large excursions of mobile ions away from the equilibrium position are enabled in the soft atomic potential and also are associated with low phonon frequencies considering the Einstein model, where the amplitude of thermal displacement u of the ion is inversely proportional to the square of the frequency ω_E using:²⁷ $\langle |u|^2 \rangle = 3k_B T / m \omega_E^2$, having k_B , T and m denote the Boltzmann constant, temperature and the mass of the mobile species, respectively. In contrast, with a high migration barrier, the mobile species oscillate close to their equilibrium position with small thermal displacement amplitude and high frequency, and have low probability of hopping to adjacent sites. The hypothesis is supported by the following observations. The self-diffusion coefficient and the activation energy of metal atoms in body center cubic metal strongly correlate with the frequency of the longitudinal acoustic mode along the $\langle 111 \rangle$ direction (at reduced wavevector $q = 2/3$), being higher with lower frequency.²⁸ Second, the computed migration enthalpy of oxygen diffusion *via* interstitialcy in rare-earth Ruddlesden–Popper phases shows strong positive correlation with reduced (more negative) force constant of the soft mode associated with the rotation of AO_6 octahedra (A = rare-earth metal ions).²⁹ Third, Wakamura has shown that the activation

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Fig. 2 Measured phonon DOS and computed total and lithium-projected phonon DOS. Experimental phonon DOS collected at 100 K are shown on top while computed phonon DOS at 0 K on the bottom as well as the computed lithium-projected DOS (shaded). (a) Li_3PO_4 (*Pnma*) (b) Li_3PS_4 (*Pnn21*) (c) $\text{Li}_{3.4}\text{Ge}_{0.4}\text{P}_{0.6}\text{O}_4$ (*Pnma*) and (d) $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ (*Pnma*). The measured phonon DOS data were obtained after background correction, optimizing lower and higher energy cut-off and details can be found in Fig. S4 (ESI[†]). The computed DOS were weighted by neutron scattering cross section of the different elements that make up the structures. The details of this procedure can be found in previous work.⁶⁷



Fig. 3 Comparison between computed and measured total phonon band centers of 7 stoichiometric LISICONs, one substituted LISICON $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ (chemically similar to $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$) and Li_4GeO_4 (*Cmcm*) at 100 K. The measured phonon band centers of LISICON $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ (*P42/nmc*) and $\text{Li}_{3.4}\text{Ge}_{0.4}\text{P}_{0.6}\text{S}_4$ (*P42/nmc*) were not included as computed phonon band centers could not be obtained due to the presence of imaginary modes in the phonon DOS of $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ and absence of refined atomic structure details of $\text{Li}_{3.4}\text{Ge}_{0.4}\text{P}_{0.6}\text{S}_4$. The computed band centers were calculated using the neutron-weighted computed DOS. The computed values are systematically lower than the experimental values, as expected from the use of the GGA functional in the calculations.

DOS for instance Li-projected DOS, we obtain the 'Lithium phonon band center' which can also be viewed as the centroid of the Li-projected phonon DOS. The stability windows were computed following the method proposed by Richard *et al.*¹⁶ using the data from Materials project database³⁹ and Pymatgen software package.⁴⁰ The stability window was computed by constructing the grand potential phase diagram and varying the chemical potential of Li until the grand potential of the electrolytes were above the convex hull.⁴¹ Measured phonon DOS of 17 LISICON and LISICON-like compounds can be found in Fig. 2–4 and Fig. S2 (ESI[†]), computed phonon DOS of some of these compounds and additional LISICONs available in the ICSD can be found in Fig. 2 and Fig. S3 (ESI[†]). The measured phonon band centers (100 K) was in excellent agreement with computed values for 7 stoichiometric LISICONs, one substituted LISICON $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ (chemically similar to $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$) and Li_4GeO_4 (*Cmcm*), as shown in Fig. 3. A systematic red shift of the computed total band center with respect to the measured total band center can be partially attributed to a well-known issue of over-estimated lattice parameters associated with GGA functional (PBE)³³ relative to measured values, giving rise to softening of high-energy modes and thus the total phonon band center.

Results and discussions

Influence of chemical substitution and temperature on phonon DOS of lithium conductors

Cation and anion substitutions in the Li_3PO_4 structural family were shown to induce systematic changes by examining measured

phonon DOS of 17 LISICON-like compounds and computed phonon DOS of 20 LISICONs. The measured and computed phonon DOS of Li_3PO_4 (*Pnma*), Li_3PS_4 (*Pnn21*), $\text{Li}_{3.4}\text{Ge}_{0.4}\text{P}_{0.6}\text{O}_4$ (*Pnma*) and $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ (*Pnma*) are shown as example in Fig. 2a–d, and those of the other LISICON-like compounds can be found in Fig. 4 and Fig. S2, S3 of the (ESI[†]). The phonon DOS measured at 100 K (the upper spectrum of each panel in Fig. 2) is in quantitative agreement with the DOS computed from DFT at 0 K (the lower spectrum). Substitution of oxygen by sulfur led to significant softening of phonon modes. Li_3PO_4 (*Pnma*) in Fig. 2a and $\text{Li}_{3.4}\text{Ge}_{0.4}\text{P}_{0.6}\text{O}_4$ (*Pnma*) in Fig. 2c were found to have higher energy phonon DOS than Li_3PS_4 (*Pnn21*) in Fig. 2b and $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ (*Pnma*) in Fig. 2d. Similar lattice softening were found for other sulfides relative to oxides in Fig. S2 and S3 (ESI[†]). Contribution from lithium ion vibrations (lithium-projected phonon DOS) in the measured total phonon DOS was identified by comparison with the computed atom-projected DOS, as shown in Fig. 2 and Fig. S3 (ESI[†]). Generally speaking, the computed phonon DOS of LISICONs show that low-energy, mid-energy and high-energy features originate mainly from the vibrations of anion sublattice, lithium sublattice and anion units involving non-mobile, structural cations (Fig. S3, ESI[†]) such as PO_4 , respectively. Of significance, Li_3PO_4 (*Pnma*) was found to have phonon DOS peaks in the range from 40–70 meV, which primarily came from lithium ion vibrations, as shown in Fig. 2a and Fig. S3 (ESI[†]). Substituting oxygen in Li_3PO_4 (*Pnma*) by sulfur to form Li_3PS_4 (*Pnma* and *Pnn21*) led to a down-shifting (softening) of lithium ion vibrations from 40–70 meV to 40–50 meV (Fig. 2b and Fig. S2, S3, ESI[†]).



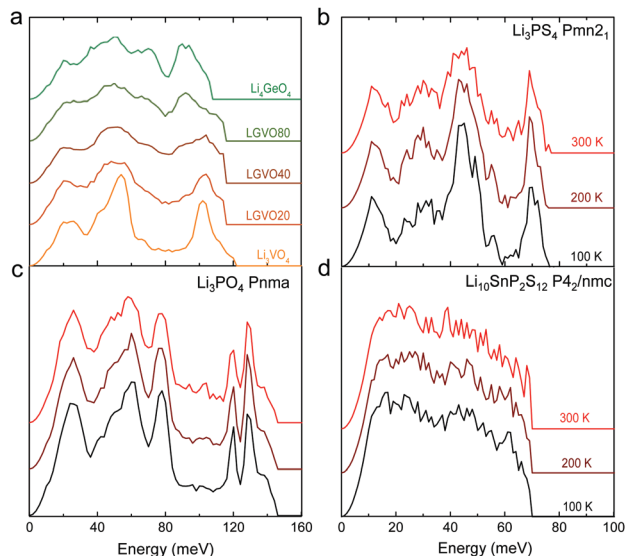




Fig. 5 (a) Comparison between measured activation energy and measured (total) band center of 7 stoichiometric LISICONs and Li_4GeO_4 (*Cmcm*), where the activation energy contains contribution from the enthalpy of defect formation and migration enthalpy, and 8 substituted LISICONs with partial occupancy, where the activation energy is essentially the enthalpy of migration. The activation energy were measured using electrical impedance spectroscopy (EIS) (Fig. S6, ESI†), and are consistent with prior work Li_3PO_4 (*Pnma*),²⁴ Li_3VO_4 (*Pmn2*),⁴⁴ Li_4GeO_4 (*Cmcm*),⁴⁵ and $\text{Li}_{3+x}\text{Ge}_x\text{V}_{1-x}\text{O}_4$ ($x = 0.2, 0.4$, and 0.6).¹⁰ Activation energy of Li_3PS_4 (*Pnm2* and *Pnma*),²⁰ Li_4GeS_4 ,¹⁹ Li_4SnS_4 ,⁶⁸ and $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ (*P4*₂/*nmc*)⁸ was taken from previous work. The blue and orange colours refer to the HT phase (space group *Pnma*) and the LT phase (space group *Pmn2*), respectively. (b) Correlation between computed enthalpy of migration and oxidation potential with computed phonon band center. The computed enthalpy of migration of 15 stoichiometric LISICONs known in the ICSD and 2 computed structures correlated well with the computed lithium band center at 0 K.

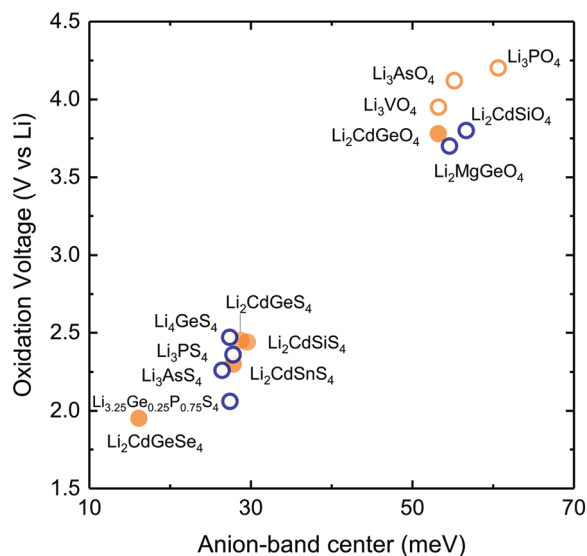
In addition, we computed the enthalpy of migration, which would allow us to systematically examine both stoichiometric LISICONs without partial occupancy and substituted LISICONs with partial occupancy. The downshifting of lithium phonon band center or average lithium ion vibration frequency was found to correlate with reduced migration barrier and thus greater lithium mobility, supporting the hypothesis described in Fig. 1a. Lithium ion migration enthalpy, which was defined as the difference between transition state energy and that of the initial/final configuration, was computed using nudge elastic band (NEB) calculations.³⁶ Identical jump sequence along the diffusion pathway shown in Fig. 5b inset was used to compute the enthalpy of lithium ion migration even though this jump sequence might not be associated with the lowest migration enthalpy. In addition to 7 stoichiometric LISICON and one substituted LISICON in Fig. 3, we included 8 others stoichiometric LISICONs in the inorganic crystal structure database (ICSD) in Fig. 5b, which represent all stoichiometric LISICONs (excluding those containing transition metals) and two computed structures ($\text{Li}_2\text{CdSiS}_4$ and $\text{Li}_2\text{CdGeSe}_4$) to complete the series of Li_2CdXS_4 ($X = \text{Si, Ge and Sn}$) and $\text{Li}_2\text{CdGeY}_4$ ($Y = \text{O, S and Se}$). Decreasing computed lithium band center of 17 stoichiometric LISICONs and one substituted LISICON $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ (chemically similar to $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$) was shown to markedly reduce the lithium ion enthalpy of migration of stoichiometric LISICON (computed) and $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ (measured activation energy) from ~ 0.85 to ~ 0.15 eV, as shown in Fig. 5b. In contrast, the correlation with the computed ligand band center (Fig. S7a, ESI†) and total band center (Fig. S7b, ESI†) was poor. Similar to the trend of total band centers (Fig. 5a), replacing oxygen with sulfur had the largest influence in downshifting the lithium band center and decreasing enthalpy of lithium ion

migration. The softening from ~ 50 meV for Li_3PO_4 (*Pnma*) to ~ 37 meV for Li_3PS_4 (*Pnma*) was correlated with a large drop in the migration barrier from ~ 0.7 eV to ~ 0.3 eV. Of significance, $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ (chemically similar to $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$) were found to have the lowest measured (Fig. 5a) and computed enthalpy (Fig. 5b) of lithium ion migration of ~ 0.2 eV, which is comparable to that of conventional liquid electrolytes used in lithium ion batteries¹ and fast lithium ion conductors such as $\text{Li}_7\text{P}_3\text{S}_{11}$,⁹ $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$,⁶ or $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$.⁷ The softened or low average lithium vibration frequency and low migration barriers found for fast lithium conductors in this study, which would facilitate more frequent successful hopping of lithium ions also favor concerted hopping⁴⁷ of lithium ions as opposed to isolated jumps in conventional ionic conductors. Therefore, computed lithium band center or the average lithium vibration frequency is proposed as one descriptor for lithium ion mobility for LISICONs and other lithium ion conductors.

Correlation between anion-band center and oxidation potential

Lowering the anion phonon band center was found to greatly reduce the stability of these LISICONs against electrochemical oxidation, as shown in Fig. 6. The oxidation potential was defined as the potential above which LISICONs will be oxidized electrochemically by lithium ion removal from the lattice, which was computed using a thermodynamic approach as reported by Richards *et al.*¹⁶ Replacing oxygen with sulfur in the LISICON structure had the largest downshift of the anion phonon band center and largest reduction in the oxidation potential. While oxidative stability can be understood in term of electronic structures of the electrolytes which correlate with the thermodynamic driving force to oxidize the materials,⁴¹ the correlation between the oxidation potential and the anion band center





shown in Fig. 6 might be kinetics in origin as lowering anion band center will make anion sublattice more mobile, thus lowering the kinetic barrier for the (decomposition) reactions. Moreover, the stability of a compound can be governed by kinetic properties (migration barriers) and thermodynamics properties. Well-known principles of understanding/controlling kinetics based on thermodynamics include the Evans–Polanyi principle or linear free energy relation, which relates the activation energy of chemical reactions (kinetics property) to the enthalpy of reactions (thermodynamics property). We believe that the correlation between the oxidation potential and anion band center is another instance of this type of ‘kinetic–thermodynamic’ relationships, which is thought in the following ways: as Li-band centers correlate with the enthalpy of lithium migration we argue that lowering the anion-band centers correlate with smaller enthalpy of anion migration (kinetic property), which promotes the kinetics of reactions. This kinetics property, by the Evans–Polanyi principle, correlates with oxidative stability (thermodynamic property) as measured by the oxidation potential. We recognize that more studies are needed to substantiate this idea. Nevertheless, we believe that this work will spur interests from the community to further explore this concept and its potential implications. Softening of the anion band center from Li_3PO_4 ($Pnm2_1$) to Li_3PS_4 ($Pnma$) by ~ 30 meV is accompanied with reduction of the oxidation potential from ~ 4 to ~ 2.5 V vs. lithium. The computed oxidation potential of Li_3PO_4 ($Pnm2_1$) and Li_3PS_4 ($Pnma$) are in agreement with previous computation.^{16,17} The computed oxidation potential of $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ is 0.21 V vs. lithium,

Of significance, fast lithium ion conductors¹⁸ based on LISiCONs such as $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ have low enthalpy of lithium ion migration and softened lithium phonon DOS, which is accompanied with downshifted anion band center (Fig. S8†, ESI†). The correlation between lowered migration barrier with softened average lithium vibration frequency in Fig. 5b, and that between lowered oxidative stability with softened average anion vibration frequency in Fig. 6 highlight a trade-off between lithium ion mobility and oxidation stability for the design of lithium ion conductors. Moreover, extending the concept in Fig. 1a to anion mobility, lowered anion band centers can be accompanied by increased anion mobility, which can promote any solid-state reaction kinetics with electrode materials. Therefore, the interplay between lattice dynamics and ion mobility and stability highlights the need and opportunities to search for fast lithium ion conductors having low lithium band center but high anion band center which exhibit high ion conductivity and high oxidative stability in lithium ion batteries.

In search of lithium ion conductors with such lattice dynamics characteristics, we further examine Olivines that have the same hexagonal anion sublattice as the LISICON structure (Fig. 7c). The computed enthalpy of lithium ion migration and lithium band center for all the stoichiometric Olivines without transition metal ions listed in the ICSD (except LiCdPO_4 , LiScGeO_4 and LiTmSiO_4) are included in Fig. 7a, which demonstrates lithium band center as descriptor for lithium ion mobility in the two structural families (LISICONs and Olivines). Olivines, exhibit low lithium band centers and migration barriers comparable to that of LISICON thiophosphates (Fig. 7a) but high anion band centers comparable to those of LISICON phosphates (Fig. 7b).



Fig. 7 (a) Correlation between computed Li-band center and the computed enthalpy of migration including the Olivine structure. (b) Anion band centers and Li-band centers of Olivine compounds compared to LISICON compounds. (c) The Olivine is closely related to the LISICON structure by the fact that both have hexagonal anion sublattice but Li occupy octahedral interstice in Olivine unlike tetrahedral sites in LISICON. The jump sequence used to compute the migration barrier as well as the minimum energy pathway associated with this jump sequence in Olivine are shown in the inset. The enthalpy of migration in olivine was found to be lower than in LISICON. All the computed enthalpies of migration were calculated using the standard climbing image nudge elastic band method⁵⁶ and the phonon band center is defined as the average phonon frequency weighted by phonon DOS. The blue and orange colours refer respectively to the HT phase (space group *Pmna*) and the LT phase (space group *Pmn2₁*), respectively while the red colour refers to the Olivine compounds. The filled circles are compounds that are known in the ICSD and/or computed in this work, where the lithium ion conductivity has not been measured experimentally. For more details, please refer to Table S1 (ESI†).

Computed migration barriers of Olivines studied here such as LiMgPO_4 are comparable to those of other Olivine materials such as LiMPO_4 ($M = \text{Mn, Fe, Co and Ni}$, 0.1–0.4 eV)⁵⁰ and LiMXO_4 (main group $M^{2+}-X^{5+}$, $M^{2+}-X^{5+}$; $M = \text{Mg, Ca, Sr, Ba, Sc, Y, Al, In, Ga}$ and rare-earth elements; $X = \text{Si, Ge, Sn, P, As and Sb}$).⁵¹ In addition, the computed migration barrier (~ 0.3 eV) of LiMgPO_4 is in good agreement with NMR measurements for the site-to-site hopping (0.3–0.5 eV).⁵² Generally speaking, while compounds having high Li conductivity tend to have low stability, Olivine family was found to be an exception to this trend, which was rationalized in terms of the low Li-band center but high anion band center in these compounds (Fig. 7b). For example, new compositions such as LiMgAsO_4 and LiInGeO_4 could potentially have high ion conductivity (Fig. 7a) and stability (Fig. S10, ESI†). Unfortunately, the one-dimensional nature of diffusion pathway in the olivine structure makes it prone to anti-site defects which can result in an apparent activation energy much higher than the intrinsic migration barrier.⁵³ For example, the long-range diffusion barrier measured by EIS for LiMgPO_4 is 0.7–1.0 eV in previous work⁵² and also in this study, much higher than the intrinsic migration barrier (~ 0.3 eV). Further studies are needed to increase the long-range ion conductivity of these Olivines by reducing anti-site defects using smaller particle sizes⁵⁴ and/or having Li-excess in the lattice,⁵⁵ which would potentially lead to the development of lithium superionic conductors with high stability against electrochemical oxidation.

Conclusion

In this study, we account for the first time, the trend in ionic mobility and electrochemical oxidation stability of lithium ion

conductors from one common physical origin, lattice dynamics, or more precisely, atomic vibrational frequencies of ion conductor constituents, thus highlighting the critical role played by the lattice dynamics in governing the lithium ion conductivity and stability of lithium-ion conductors. Unlike previous studies on lattice dynamics in ion conductors (especially Ag^+ conductors) which focus on the total phonon DOS (such low-energy peak in $\alpha\text{-AgI}$ phonon DOS) or zone-center phonons as measured from infrared and Raman spectroscopy,^{56,57} our study clarifies the influence of lattice dynamics on ionic conductivity by separating the effect of different sublattice and in particular the special role of the mobile species sublattice dynamics in the observed ionic mobility. The phonon DOS have been collected from a series of lithium conductors in the LISICON family using INS and computed by first-principles simulations to identify specific spectral features corresponding to the vibrations of sublattices involving lithium, anion and nonmobile structural cations. Replacing oxygen with sulfur greatly downshifts the lithium vibration frequencies while aliovalent cation substitution tends to broaden the lithium vibrational features in the phonon DOS. We show that low vibration frequencies of lithium ions correlate with enhanced lithium ion mobility in the LISICON and Olivine families, which can be used as one lithium ion mobility descriptor to predict new fast lithium conductors. Recent work on Argyrodite lithium conductors also showed the influence of lattice dynamics on the ionic conductivity.⁵⁸ Future work is needed to define a more refined descriptor that would take into account not only the vibration frequency but also the vibrational pattern of each mode and weight in a way that reflects its importance to lithium diffusion as the measured and computed band centers or the average vibrational frequencies



determined in this study do not explicitly take into account the specific vibration pattern of each mode. In addition, future experimental and computational studies should exploit the interplay between lattice dynamic and ion conductivity and stability for lithium ion conductors of different structural families²¹ beyond LISICON and Olivine. Moreover, further studies are needed to extend and examine the universality of such descriptors based on lattice dynamics to understand and potentially control ion mobility and stability of other ionic conductors such as Na⁺, Cu⁺ or O²⁻ conductors. For example, copper sulfide (Cu_{2-x}Se) with superionic Cu⁺ conductivity at room temperature is known to have low-energy phonon DOS and lattice thermal conductivity.⁵⁹ Lattice dynamics was also found to play important role in the Na⁺ conductors Na₃PS_{4-x}Se_x⁶⁰ as well as O²⁻ conductors Nd₂NiO_{4+δ}⁶¹ and brownmillerites Sr(Fe,Co)O_{2.5}.⁶² Lastly, although extensive database for material phonon DOS is not yet available due to high computational cost to compute phonon DOS, recent study has shown that it is possible to use a machine learning model to predict phonon-related properties such as vibrational free energy and entropy with high accuracy at a greatly reduced computational cost.⁶³ Future advance in machine-learning computational material design represents an exciting opportunity to use this approach to explore more compositional space and to discover new ion conductors.^{64–66}

Author contributions

S. M., Y. S.-H. and J. C. B. proposed the concept. J. C. B. and H.-H. C. prepared the oxide materials. R. K. provided the sulphides samples. S. M., J. C. B., D. B. and O. D. performed the phonon DOS measurements and analysis. S. M. performed all the DFT calculations with L. G.'s help for the NEB calculations. S. M. and Y. S.-H. wrote the manuscript. All authors contributed to the discussion and revision of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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