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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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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}



energy in Ag^+ , Na^+ , Cu^+ and F^- superionic conductors decreases with decreasing frequency of low-energy optical mode³⁰ supporting the idea that low phonon frequency can be associated with high probability of ions hopping to the neighboring sites.²¹

We elected to study a series of lithium ion conductors in the LISICON family derived from Li_3PO_4 , to test the hypothesis that their lattice dynamics can greatly influence lithium ion mobility and stability. Lithium ion conductivity can be increased by up to 15 orders of magnitude^{10,11,18,20,21} via cation and anion substitutions in this structural family relative to Li_3PO_4 (Fig. 1d). We also included Olivine structure which has the same (distorted) hexagonal close packed of anion sublattice as the LISICON compounds but differ in occupancy of Lithium ions which are located in octahedral sites as opposed to tetrahedral sites in LISICON structure. Although substitution (doping) and defects may alter migration pathway and mechanism and the activation energy, we have selected lithium ion conduction in LISICON and Olivine, having similar one-dimensional channels of Li ions within hexagonal anion sublattice. Previous work has shown that in Olivine, these one-dimensional channels serve as the dominant pathway for lithium migration and govern ion conduction in this structure.⁵⁰ In Lisicon, although the diffusion pathway is three-dimensional,³¹ previous study has shown that the enthalpies of vacancies migration along each crystallographic direction are very similar and on the order of 0.7 eV in both $\gamma\text{-Li}_3\text{PO}_4$ and $\beta\text{-Li}_3\text{PO}_4$.³² It should be mentioned that depending on the concentration of mobile specie, the dominant diffusion mechanism might be interstitial instead of vacancy diffusion considered here. Nevertheless, we believe that the trends that we propose here remain valid as long as one considers the same mechanism with similar diffusion pathway regardless of the compound chemistries and structures. Isovalent substitution of oxygen by sulfur anion can enhance the ionic conductivity by six orders of magnitude, having reduced activation energy from 1.3²⁴ to 0.52 eV,²⁰ and additional four orders of magnitude by aliovalent substitution of phosphorus by germanium, with decreasing activation energy from 0.52 to 0.21 eV.¹⁸ In this work, we systematically study the lattice dynamics of LISICONS derived from Li_3PO_4 by measuring the phonon density of states (DOS) of 17 compounds and one olivine compound as well as computing the phonon DOS of more than 20 compounds which are isostructural to LISICON and 6 olivines. The reader is referred to the Table S1 in (ESI†) for a complete list of compounds included in this study. From these data, combined with the measured activation energy, computed enthalpy of lithium ion migration of LISICONS and computed potential for electrochemical oxidation, the descriptors for lithium ion mobility and stability for oxidation were proposed.

Experimental and computation methods

All phonon DOS measurements were made at the Wide-angular range chopper spectrometer (ARCS) at the Spallation Neutron

Source at Oak Ridge National Labs. Approximately 5 g of the samples were packed into aluminum canisters, which were sealed with a vanadium ring, unless spectra at elevated temperatures were measured where a qualitative (aluminum on aluminum) seal was used. All samples were sealed under argon. Temperatures were varied from 10 K to 600 K for select samples. Unless otherwise noted, the samples were measured at 100 K. The incident neutron energies were varied between 60, 100, and 200 meV. The resulting data were analyzed using the Mantid DGS Reduction package. For oxides, the background fraction was set as 1, the fraction of the total scattering to subtract as a constant background was 0.0–0.25 unless otherwise noted, the cutoff for the elastic peak removal was set as 10 meV, 3 bins after the cutoff were averaged to get the value of the density of states near the cutoff, the estimate of the Debye cutoff and the limit on the energy range were set depending on the calculated phonon density of states and where the last feature in the experimental density of states was noted (these parameters were used to remove any high energy background), and the range in wave vector that was used was from 7–12 \AA^{-1} . For sulfides, the parameters were the same except the range of wave vectors used was from 4–9 \AA^{-1} .

For computations, we used density functional theory based on the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation³³ as implemented in the VASP package.³⁴ The core electrons were treated within the Projector Augmented Wave (PAW) method.³⁵ Migration barriers for a lithium ion hopping were calculated using the climbing-image nudged elastic band method³⁶ in a $2 \times 2 \times 1$ supercell for LISICON (space group $Pnma$) while for the LISICON (space group $Pnm2_1$), a $2 \times 2 \times 2$ supercell was employed. A $2 \times 2 \times 2$ k -point grid was used and the cutoff of the kinetic energy was set to the default values as set in the pseudopotential files. For phonon calculations, the same supercells were used with finer k -point grid ($3 \times 3 \times 3$) and a higher energy cutoff (520 eV) in order to obtain more accurate values of the force. We have also used a higher cut-off energy of 700 eV for phonon DOS calculations but haven't found any significant change (Fig. S1, ESI†) indicating that phonon DOS calculations are already well converged at 520 eV of cut-off energy. We have also tested LDA functional for phonon DOS calculations and found that the main effect of is to shift all the modes especially the high-energy feature in the DOS to higher frequencies resulting in an upward shift of band center (Fig. S1, ESI†) in agreement with previous study.³⁷ However, the magnitude of the shift is small and fairly constant across different chemistries and crystal structures suggesting that LDA functional will result in a rigid shift to slightly higher energy but will not affect the trend. Finite displacement method was used for phonon calculations and the total as well as the atom-projected DOS were extracted using the phonopy package.³⁸

To quantify the average vibrational frequency of a given material, we defined the 'phonon band center' which is the phonon frequency weighted by the DOS. Mathematically, it is written as:

$$\omega_{\text{av}} \equiv \frac{\int \omega \times \text{DOS}(\omega) d\omega}{\int \text{DOS}(\omega) d\omega}$$

If we replace $\text{DOS}(\omega)$ in this expression by the total phonon DOS, we obtain what we called 'total phonon band center'. Similarly, if we replace $\text{DOS}(\omega)$ by one of the atom-projected





Fig. 4 Measured phonon DOS as function of aliovalent substitution and temperature. (a) Measured phonon DOS of the series $\text{Li}_{3+x}\text{Ge}_x\text{V}_{1-x}\text{O}_4$ ($x = 0, 0.2, 0.4, 0.8$ and 1) (abbreviated as LGVO20, LGVO40 and LGVO80 for $x = 0.2, 0.4$ and 0.8 respectively) measured at 100 K. (b) The phonon DOS of Li_3PS_4 ($Pnm2_1$) measured at 100, 200 and 300 K, which shows marked broadening at ~ 50 meV. (c) The phonon DOS of Li_3PO_4 ($Pnma$) measured at 100, 200 and 300 K, which shows little variation with temperature. (d) The phonon DOS of $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ that are featureless measured at 100, 200 and 300 K. 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 †).

Aliovalent cation substitution induces broadening of features in the phonon DOS, without significant softening. Phonon peaks, including the peak that primarily came from lithium ion vibrations in the range from 40–70 meV, was broadened systematically with increasing Ge substitution in $\text{Li}_{3+x}\text{Ge}_x\text{V}_{1-x}\text{O}_4$, where $x = 0, 0.2, 0.4, 0.8$ and 1 (Li_3VO_4 , LGVO20, LGVO40, LGVO80 and Li_4GeO_4) in Fig. 4a. Similar broadening of lithium phonon DOS was observed for $\text{Li}_{3.4}\text{Ge}_{0.4}\text{P}_{0.6}\text{O}_4$ ($Pnma$) and $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ ($Pnma$) upon substituting P with Ge in Li_3PO_4 ($Pnma$) and Li_3PS_4 ($Pnm2_1$), respectively, as shown in Fig. 2. On the other hand, isovalent cation substitution by heavier ions such as replacing P with V in Li_3PO_4 (Fig. S5a, ESI †) led to minimal downshifting of lithium band center but large downshifting of high-energy phonon modes involving non-mobile, structural cations, to the extent which shared similar energy to lithium phonon DOS in the case of sulfides (Fig. S5b, ESI †). Therefore, the broadening of lithium ion vibrations can be attributed to increasing disorder by introducing defects into the LISICON structure⁴² such as increasing partial occupancy in the lithium sublattice. This hypothesis is supported by marked broadening of lithium phonon modes observed for Li_3PS_4 upon increasing temperature from 100 K to 300 K while remaining phonon DOS features of less mobile PS_4 units in Li_3PS_4 showed negligible changes, as shown in Fig. 4b. This broadening can be explained by greater lithium partial occupancy and large displacement amplitudes (anharmonicity)⁴² of lithium ions in Li_3PS_4 as expected from its low migration barrier (~ 0.5 eV), in agreement with the concept discussed

in Fig. 1a. Further support came from the observation that no broadening of lithium vibration modes at ~ 50 meV was noted for Li_3PO_4 (Fig. 4c), since the partial lithium occupancy (or mobile lithium ion concentration) is low ($\sim 2.05 \times 10^8 \text{ cm}^{-3}$ at 300 K using lithium vacancy formation energy of ~ 1.7 eV),⁴³ and small displacement amplitudes. Furthermore, $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ (isostructural to $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$), with disordered lithium sublattice and liquid-like lithium ion conductivity at room temperature,⁸ was found to have phonon DOS so broadened that no peak feature was visible, which did not change upon heating from 100 to 300 K, as shown in Fig. 4d.

Correlation between Li-band center and enthalpy of migration

Softening of phonon DOS for LISICONs was found to correlate with decreasing measured activation energy for lithium ion conductivity. Increasing temperature has negligible influence on this phonon band center, which is supported by temperature-dependent phonon DOS in Fig. 4b and c, showing no softening of phonon frequencies with increasing temperature. Downshifting the total phonon band center was shown to markedly lower measured activation energy of stoichiometric LISICONs, as shown in Fig. 5a. Replacing oxygen with sulfur from Li_3PO_4 ($Pnm2_1$) to Li_3PS_4 ($Pnm2_1$) led to the largest downshift of the total phonon band center from ~ 70 to ~ 40 meV, which was correlated with reduction of activation energy from 1.4 eV²⁴ to 0.5 eV²⁰ in Fig. 5a. Measured activation energy of Li_3PO_4 ($Pnma$), Li_3VO_4 ($Pnm2_1$), $\text{Li}_{3.4}\text{Ge}_{0.4}\text{P}_{0.6}\text{O}_4$ ($Pnma$) and $\text{Li}_{3+x}\text{Ge}_x\text{V}_{1-x}\text{O}_4$ ($x = 0.2, 0.4, 0.6$ and 1) obtained in this study are in agreement with previous EIS measurements.^{10,24,44,45} As the measured activation energy of stoichiometric LISICONs consists of both enthalpy of defect formation and enthalpy of migration, such a correlation for stoichiometric LISICONs does not explicitly imply lowered lithium migration barrier with softening of the total phonon band center. We further show that the measured activation energy for 8 substituted LISICONs with partial lithium occupancy, which corresponds largely to lithium ion migration enthalpy, was decreased with softening of the total phonon band center. $\text{Li}_{3.4}\text{Ge}_{0.4}\text{P}_{0.6}\text{S}_4$ ($P6_2/nmc$) and $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ (chemically similar to $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$), $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ ($P6_2/nmc$)⁸ were found to have the lowest activation energy of ~ 0.25 eV comparable to best superionic conductors^{6–9} with the lowest measured total band centers of ~ 40 meV. Another interesting observation that we can draw from Fig. 5a is the clear separation between stoichiometric and non-stoichiometric compounds which follows two distinct trend lines whose difference is essentially related to the enthalpy of defect formation. It is well-known in perovskites that the enthalpy of migration of oxygen ions decreases with decreasing enthalpy of vacancy formation.⁴⁶ Although, in this study, we do not consider the energetic of lithium defect formation energy, in light of the data shown in Fig. 5a, one might hypothesize that the enthalpy of Lithium defect formation might also correlate with phonon band center.

As the total phonon band center can be weighted considerably for the vibrations of non-mobile species such as structural cations and anions, we further sought correlations between the band center of lithium-projected phonon DOS and activation energy.





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 (*Pmn2₁*),⁴⁴ Li_4GeO_4 (*Cmcm*),⁴⁵ and $\text{Li}_{3+x}\text{Ge}_x\text{V}_{1-x}\text{O}_4$ ($x = 0.2, 0.4, \text{ and } 0.6$).¹⁰ Activation energy of Li_3PS_4 (*Pnm2₁* and *Pnma*),²⁰ Li_4GeS_4 ,¹⁹ Li_4SnS_4 ,⁶⁸ and $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ (*P4₂/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 *Pmn2₁*), 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 LISICONS and one substituted LISICONS 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 LISICONS $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ (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 LISICONS (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 LISICONS 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



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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