Influence of Lattice Dynamics on the Ionic conductivity and Stability of Solid-State Lithium-Ion Conductors

by

Sokseiha Muy

Submitted to the Department of Materials Science and Engineering in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the MASSACHUSETTS INSTITUTE OF TECHNOLOGY June 2018

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ABSTRACT

Electrochemical energy storage devices are clean and efficient, but their current cost and performance limit their use in many transportation and stationary applications. Lithium-ion batteries are one of the leading candidates for these large applications, however their current use of liquid electrolytes negatively effects their lifetime and safety. Furthermore, the liquid electrolyte's potential stability window, thermal stability, and volatility are of particular concern in these large-scale applications. Solid-state electrolytes are investigated as one of the best solutions to overcome these challenges. However, the ionic conductivity and especially (electro)chemical stability of many solid electrolytes are still problematic.

The focus of this thesis is on ionic mobility and stability of solid-state Li-ion conductor and descriptors that correlates with these properties. We first provide a comprehensive review of several important families of Li-ion conductors that have been studied and published in the literature focusing on their and an overview of some descriptors that have been proposed to correlate with the ionic conductivity/activation energy, for instance, the volume of the diffusion pathway, high-frequency dielectric constants and frequencies of low-energy optical phonons.

Build upon these previous understandings, we propose a new approach to understand ion mobility and stability against of lithium insertion/removal in ion conductors based on lattice dynamics. By combining inelastic neutron scattering measurements with density function theory computation, greater lithium ion mobility was correlated with decreasing lithium vibration frequency that was quantified using a newly proposed descriptor which we phonon band centers. Known superionic lithium conductors were shown to have not only low lithium phonon center but also low anion phonon band center, which unfortunately reduces stability against electrochemical oxidation. 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 (electro)chemical stability in lithium ion batteries. We show and discuss that Olivines with low lithium band centers but high anion band centers are particularly promising to explore for lithium ion conductors with high ion conductivity and stability. With this new approach, we were able for the first time to account for the trend in ionic conductivity and electrochemical oxidation stability of lithium ion conductors from one common physical origin, their lattice dynamics. Such findings open new avenues for the discovery of new lithium ion conductors with enhanced conductivity and stability using lattice dynamics.
Finally, to study the correlation between the activation energy and the pre-exponential factor, the ionic conductivity and activation energy of lithium in the Li₃PO₄-Li₃VO₄-Li₄GeO₄ system was systematically investigated as model system. The sharp decrease in activation energy upon Ge substitution in Li₃PO₄ and Li₃VO₄ was attributed to the reduction in the enthalpy of defect formation while the variation in activation energy upon increasing Ge content was rationalized in term of the inductive effect. The series of compound with and without partial lithium occupancy were shown to fall into two distinct lines whose slope was related to the inverse of the energy scale associated with phonon in the systems according to multi-excitation entropy theory and the intercept to the Gibbs free energy of defect formation. Compiled data of pre-exponential factor and activation energy for commonly studied Li-ion conductors shows that this correlation is very general, implying an unfavorable trade-off between high pre-exponential factor and low activation energy needed to achieve high ionic conductivity.

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Table of Contents

1. Introduction ......................................................................................................................... 11
   1.1 Anatomy of Li-ion battery ......................................................................................... 11
   1.2 The advantages and challenges associated with the use of solid-state electrolytes .... 14
   1.3 Outline of the thesis ................................................................................................. 15

2. Factors Influencing Ionic Conductivity in Solid-State Lithium Electrolytes ................. 17
   2.1 Fundamental of ionic diffusion in liquid and solid electrolytes ............................... 17
   2.2 Solid-state Li-ion conductors .................................................................................. 22
      2.2.1 Lisicon (Lithium superionic conductors) ......................................................... 23
      2.2.2 Garnet family .................................................................................................. 24
      2.2.3 Perovskite family ............................................................................................ 26
      2.2.4 Nasicon-like family ........................................................................................ 27
      2.2.5 Argyrodite family .......................................................................................... 28
   2.3 Crystal-structure based descriptor for activation energy ........................................... 29
      2.3.1 Volume of the unit cell ................................................................................. 29
      2.3.2 Mechanical strain ........................................................................................ 31
      2.3.2 Volume of diffusion pathway ........................................................................ 33
   2.4 Polarizability of the anion sublattice ......................................................................... 36
   2.5 Lattice dynamics ....................................................................................................... 38

3. Influence of Lattice Dynamics on Ionic Conductivity and Stability in Solid-State Lithium Conductors .............................................................................................................................. 40
   3.1 Intuitive understanding of the relationship between lattice dynamics and migration barrier ............................................................................................................................................. 40
   3.2 Lisicon and olivine as model systems ....................................................................... 42
   3.3 Variation of Phonon Density of States (DOS) with temperature, chemical substitution and concentration of mobile specie ................................................................................. 46
   3.4 Correlation between phonon band center and migration barrier ............................... 50
      3.4.1 Phonon band center ....................................................................................... 50
      3.4.2 Calculation of migration in Lisicon and Olivine families ................................. 52
      3.4.3 Results and discussions ............................................................................... 54
   3.5 Correlation between phonon band center and (electro)chemical stability of Li-ions conductors...................................................................................................................... 55
      3.5.1 Computation of stability window of solid state Li-ion conductors ................ 55
      3.5.2 Results and discussions ............................................................................... 59

4. Lattice Dynamics and Meyer-Neldel Rule in Li₃PO₄ - Li₃VO₄ - Li₄GeO₄ System .......... 64
   4.1 Li₃PO₄ - Li₃VO₄ - Li₄GeO₄ solid solutions as model system ....................................... 65
      4.1.1 Material synthesis and characterizations ......................................................... 65
4.1.2 Lithium Ion conductivity of Li$_{3}$P$_{1-x}$V$_{x}$O$_{4}$, Li$_{3+x}$V$_{1-x}$Ge$_{x}$O$_{4}$ and Li$_{3+x}$P$_{1-x}$Ge$_{x}$O$_{4}$ (x = 0, 0.2, 0.4, 0.6, 0.8 and 1) ................................................................. 67
4.1.3 Classical Molecular dynamics simulations of Li$_{3+x}$V$_{1-x}$Ge$_{x}$O$_{4}$ (x = 0.2, 0.4, 0.6, 0.8 and 1) .............................................................................................................. 69

4.2 Meyer-Neldel Rule in Li-ion conductors............................................................ 73
4.2.1 Observation of Meyer-Neldel behavior in Li$_{3}$PO$_{4}$ - Li$_{3}$VO$_{4}$ - Li$_{4}$GeO$_{4}$ ................................................................. 73
4.2.2 Physical origin of the Meyer-Neldel Rule and the physical interpretation of the intercept in the Meyer-Neldel plot ................................................................. 74
4.2.3 Extension to other Li-ion conductors ................................................................ 78

5. Conclusions and Outlooks ..................................................................................... 82
5.1 Influence of lattice dynamics in other ionic conductors ........................................ 84
5.2 Issue with Olivine compounds as Li-ion conductors ........................................... 84
5.3 High-throughput computation of phonon DOS and stability of Li-ion conductors ... 87
5.4 Meyer-Neldel Rule in Lithium conducting polymers ........................................... 91

Appendix .................................................................................................................... 94
A. Computation of phonon DOS and migration barrier ........................................... 94
   A.1 Density Functional Theory calculations ......................................................... 94
   A.2 Classical Molecular Dynamics Calculations .................................................. 96
B. Phonon DOS measurements .................................................................................. 97
   B.1 Phonon DOS extractions ............................................................................... 97
   B.2 Measured phonon DOS .................................................................................. 101
C. Material synthesis and characterizations ............................................................. 106
   C.1 Synthesis of oxide compounds ...................................................................... 106
   C.2 Synthesis of sulfide compounds .................................................................... 106
   C.3 Material characterizations .............................................................................. 109
D. EIS measurements of ionic conductivity ............................................................. 111
E. Computed Phonon Density of States .................................................................... 114
   E.1 Phonon DOS of stoichiometric compounds .................................................. 114
   E.2 Phonon DOS of non-stoichiometric compounds ........................................... 115

References .................................................................................................................. 126
Chapter 1

Introduction

The advent of Li-ion battery (LIB)\textsuperscript{1-7} has led to widespread adoption of portable electronic devices such as smart phones, laptops, cameras just to name a few.\textsuperscript{8} The next frontier of Li-ion technology development will target the mobility and energy sectors or more precisely battery that will power electric vehicles\textsuperscript{9} and store electricity generated from renewable sources such as solar and wind power.\textsuperscript{10} These new markets come with major challenges associated with the safety, performance, lifetime and cost of the battery. Currently, significant research effort has been devoted to the optimization of the existing technology and finding new chemistry for electrodes and electrolytes that can reduce the cost of the battery while maintaining or even improving the energy and performance of the battery.\textsuperscript{11,12}

1.1 Anatomy of Li-ion battery

A battery is one type of energy-storage device that converts electricity to chemical energy during charge and chemical energy back to electricity during discharge. It typically consists of a positive electrode (cathode), a negative electrode (anode) separated by an electrolyte which must be electronically insulating but ionically conducting. In a conventional Li-ion battery (Figure 1.1),\textsuperscript{13} the positive electrode is in general a lithium-containing transition metal oxide such as LiCoO\textsubscript{2},\textsuperscript{14} LiFePO\textsubscript{4},\textsuperscript{15} or the NMC series (LiNi\textsubscript{x}Mn\textsubscript{y}Co\textsubscript{z}O\textsubscript{2}, x+y+z=1)\textsuperscript{16}. The negative electrode is typically graphite and the electrolyte an organic solvent in which a lithium salt is dissolved (typically a mixture of Ethylene carbonate (EC) and Dimethyl carbonate (DMC) in 1:1 ratio in which 1M of LiPF\textsubscript{6} salt is dissolved). During charge, Li-ions are removed from the positive electrode, shuttled through the electrolytes and finally intercalated into the graphite anode. During discharge, this process is reversed. The energy stored in a battery depends on two factors: the voltage at which the battery operates and the capacity which is the number of Li that the battery can store per unit weight (gravimetric density) or volume (volumetric density).\textsuperscript{17} Ideally, we would
Figure 1.1 Schematic of a conventional Li-ion battery. The negative electrode is made of graphite while the positive electrode is a Li-containing transition metal oxide. The electrolyte is an organic solvent in which a Li salt is dissolved.\textsuperscript{13}

like to maximize these two quantities so that the battery can store a maximum amount of energy (or electricity). In practice, we are limited by the electrodes and electrolytes that are at our disposition. Figure 1.2 is a nice illustration of the voltage and capacity that be obtained for different materials that are current used in LIB or being actively developed for the next generation of LIB.\textsuperscript{1} Layered transition metal oxides cathodes typically operate at $\sim 4V$ vs Li/Li\textsuperscript{+} and have a (theoretical) capacity around 200 Ah/Kg. Graphite anode operates at $\sim 0.2-0.3V$ vs Li/Li\textsuperscript{+} with a capacity of $\sim 300$ Ah/Kg. Cathode materials with higher voltage such as spinel LiNi\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4} which can reach over 5V vs Li/Li\textsuperscript{+} are currently being developed although outstanding issues such as capacity fading upon cycling still await a satisfactory solution.\textsuperscript{18} On the negative electrode, the ultimate goal would be a Li anode which has an impressive capacity of $\sim 3800$ Ah/Kg, more than one order of magnitude higher that graphite. However, pairing a high-voltage cathode with a Li
metal anode in a full cell battery remains challenging as several complications occurs during the battery operation. First, the organic solvent used as the electrolyte medium may not be (kinetically) stable at such high voltage. As a result, the electrolytes can decompose, leading to a drastic capacity fading during cycling. Second, upon charging, it was found that Li instead of depositing in a smooth layer, form dendrites that grow upon cycling. This dendritic growth eventually leads to a short circuit, which combined with the highly flammable nature of the organic solvents, can lead to potential hazard such battery catching fire which has to be avoided at all cost. As we will discuss below, replacing liquid electrolytes by a solid Li-ion conductor have the potential to mitigate if not completely eliminated this hazard with added benefit of enabling the use of Li metal as anode without dendrite formation. Moreover, the solid nature of Li-ion conductors avoids the need of sophisticated packaging required to avoid leakage of liquid electrolytes, therefore allows a more compact battery with higher energy density. Thanks to all of this advantage, huge amount of research both in academia and industries have been devoted to the design and fabrication of new solid Li electrolytes which can be used in the next generation of LIB.
The advantages and challenges associated with the use of solid-state electrolytes

Due to their relatively high Young modulus compared to liquid electrolytes, the use of solid electrolytes is believed to prevent dendrite formation that can lead the short circuit of the battery. Moreover, all known solid Li-ion conductors are non-flammable therefore eliminating of the risk catastrophic fire as can occur with flammable organic solvents. The main challenge associated with solid Li-ion conductors has long been the low ionic conductivity in these materials which can negatively impact the rate capability of the battery. However, since the ground-breaking discovery of superionic conductor Li_{10}GeP_{2}S_{12} by Kanno and co-workers in 2012, many Li-ion conductors having ionic conductivity comparable or even exceeding that of EC-DMC 1:1 LiPF_{6} have been synthesized.\textsuperscript{26} Unfortunately, while low ionic conductivity issue can be considered as 'solved', an all solid-state Li-ion battery still has a long to go (with the exception of LiPON micro-battery\textsuperscript{27}) has a long way to go before a large-scale commercialization. The problem is ionic conductivity is just one of many performance metrics that a material needs to meet in order to be
used as a solid electrolyte. Figure 1.3 shows some of these metrics including stability (thermal and (electro)chemical), mechanical properties, ion selectivity, conductivity (electronic and ionic) as well as the ease of processing and device integration of several commonly studied Li-ion conductors. The structures and properties of these families of Li conductors will be discussed extensively in the next chapter. For now, it is sufficient to note that, none of these families meet all the requirement to be used in all solid-state battery. Oxides for examples have reasonably high ionic conductivity and good stability. However, the oxide ceramics tend to be brittle (poor mechanical property) and require high temperature for the synthesis which make cost and device integration challenging. On the other hand, Sulfides have excellent ionic conductivity and can be synthesized at relatively low temperature but suffer from poor (electro)chemical stability. The quest to find the ideal material(s) that satisfy all of these criteria is a daunting one and remains largely open. It is conceivable that the eventual all-solid battery that will eventually be commercialized contained not one but 2 or 3 different electrolytes that works synergistically to produce the best performance. In this thesis, we focus on two metrics in particular namely ionic conductivity and (electro)chemical stability. The detail of the research plans and methods is given in the next section.

1.3 Outline of the thesis

The main objective of this thesis is to propose a new design principle or a descriptor which account for ionic conductivity and stability on the same footing. Moreover, we would like to have a descriptor that is as general as possible, namely it can be used across different crystal structures and chemistries instead of focus on a single family of Li-ion conductors. The questions of mobility and stability are addressed from the perspective of lattice dynamics which can be described by the phonon density of states (DOS). We combine experiments (electrochemical impedance spectroscopy (EIS) and inelastic neutron scattering (INS)) and computations (density functional theory (DFT), classical molecular dynamics (MD) and nudge elastic band calculation (NEB)) in order to elucidate the factors that govern the stability and mobility of Li-ion in solid-state Li-ion conductors. In the second chapter, a thorough overview of different Li-ion conductors families is presented. Their crystal structures and their properties will be described in detailed. Particular emphasis will be put on their ionic conductivity as well as several descriptors that have been previously proposed in the literature in order to explain the trend in ionic conductivity/activation
energy found in those systems. We will classify these descriptors as crystal structure-based or electronic structure based and discuss their applicability and limitation in predicting new compositions. Finally, we will introduce a new family of descriptor based on lattice dynamics and will expand upon this in more detail in chapter 3 by focusing more specifically on Li-ions conductors. In chapter 3, we will also introduce basic idea which will lead us to the desired lattice-dynamic based descriptor for the enthalpy of migration and the electrochemical stability. In chapter 4, we will turn our attention to the other knob to tune the ionic conductivity which is the pre-exponential factor. We will specifically focus on the Li$_3$PO$_4$-Li$_3$VO$_4$-Li$_4$GeO$_4$ system in which the ionic conductivity as a function of substitution is systematically investigated. We found a correlation between the pre-exponential factors and the activations in agreement with the well-known Meyer-Neldel rule. The series of compound with and without partial lithium occupancy were shown to fall into two distinct lines whose slope was related to the inverse of the energy scale associated with phonon in the systems according to multi-excitation entropy theory and the intercept to the Gibbs free energy of defect formation. We also present a compilation of pre-exponential factor and activation energy data for commonly studied Li-ion conductors and shows that this correlation is very general, implying an unfavorable trade-off between high pre-exponential factor and low activation energy needed to achieve high ionic conductivity. Finally, in chapter 5, a summary of the main findings of this thesis is presented and the outlook for future research and the implication of the proposed descriptors and new understandings are discussed.
Chapter 2

Factors Influencing Ionic Conductivity in Solid-State Lithium Electrolytes

In this chapter, we will be reviewing the fundamental of ionic diffusion in solid and liquid electrolytes as well as a detail discussion of many important lithium ion conductors that have been discovered in the last several decades. We will in particular introducing the Arrhenius equation that governs the ionic conductivity in crystalline and amorphous materials. This provides us an occasion to discuss several important parameters such as pre-exponential factor, activation energy and mobile charge carrier concentration which will be useful for the discussion of various descriptors which have been proposed to explain the variation of ionic conductivity but will also set the stage for the discussion that will be covered in the next two chapters.

2.1 Fundamental of ionic diffusion in liquid and solid electrolytes

The ionic diffusion in solid-state electrolytes is very different from that in liquid electrolytes. In liquid electrolytes, the diffusing species, in this Li⁺, are solvated by the solvent molecules and the diffusion involves solvation/de-solvation of the Li⁺ as it moves through the solvent media. Because the time scale of solvent exchange (the time over which Li-ions are solvated and de-solvated) is relatively small compared to the time scale of diffusion, the potential energy landscape as ‘seen’ by the mobile specie can be considered as flat (Figure 2.1). To increase the ionic conductivity in liquid electrolytes, one can use a solvent with lower viscosity to promote the mobility of the ions and/or higher dielectric constant with stronger dissociation power allowing a higher concentration of salt to be dissolved and hence increase the concentration of mobile ions. In contrast, in solids, due to the regular arrangement of ions forming the lattice, the mobile species experience regular potential energy landscape with minima (corresponding to equilibrium positions) and maxima (corresponding to the bottleneck or transition state) along its diffusion
Figure 2.1 Arrhenius plot of Li-ion conductivity for several classes of Li-ion conductor: ionic liquid (LiBF₄/EMIBF₄), organic solvent (EC:DMC 1M LiPF₆), polymer (PEO-LiClO₄), glass (LiPON) and the rest are crystalline materials. On the right, the schematics of Li environment in liquid and solid electrolytes and the expected potential energy landscape. Adapted from ref. 29.

Pathway (Figure 2.1). The energetic barrier, defined as the difference between the maxima and minima along the diffusion pathway is called migration barrier generally denoted as $E_m$. This energy barrier can greatly influence ionic mobility and ionic conductivity, where low $E_m$ leads to high ionic mobility and conductivity.

Similarly, the ionic conductivity of crystalline materials also depends on the concentration of mobile species which can be interstitial ions (Frenkel defects) or vacancies (associated with Schottky defects in lattice sites or interstices, and which is determined by defect formation energy, $E_f$, (or more precisely the Gibbs free energy of defect formation $G_f$).³⁰ In stoichiometric ion conductors, i.e. material with partial occupancy, the concentration of mobile charge carriers is thermally activated (known as the intrinsic regime) and is typically very low. The defect formation energy $E_f$ can be significantly reduced and so, interstitials or vacancies concentration can be increased dramatically by aliovalent substitution (extrinsic regime). In this regime, the
concentration of mobile specie can also depend on the interaction between dopants and defects, whose formation energetics is governed by the trapping energy $E_t$ which can lead to complex behavior such as defect clustering. In both intrinsic and extrinsic regimes, the apparent activation energy $E_A$ of ion conductivity contains both contributions from the defect formation energy $E_f$ or $E_t$, and migration energy $E_m$.

Generally speaking, ionic conductivity in a crystalline solid is the product of the number of mobile lithium ions per unit volume $n$, the square of the elementary charge $e$ of each mobile ion and its mobility $\mu$:

$$\sigma = n e^2 \mu$$  \hspace{1cm} (2.1)

The concentration of mobile species is related to the defect formation energy $E_f$ by:

$$n = n_0 \exp \left( -\frac{E_f}{2k_BT} \right)$$  \hspace{1cm} (2.2)

Where $n_0$ is the maximum concentration of the mobile species, $T$ the temperature in Kelvin, and $k_B$ the Boltzmann constant. The mobility $\mu$, can be related to the lithium diffusion coefficient in the considering non-interacting lithium ions, the lithium-ion mobility, $\mu$, can be related to the lithium diffusion coefficient $D$ by the Nernst-Einstein equation:

$$\mu = \frac{D}{k_BT} \quad \text{and} \quad D = D_0 e^{\frac{E_m}{k_BT}}$$  \hspace{1cm} (2.3)

with $D_0$ is a constant depending several microscopic parameters such as jump length, jump frequency... which will be discussed in more in chapter 4. Combining (2.1), (2.2) and (2.3), the ionic conductivity can be expressed as:

$$\sigma = \frac{\sigma_0}{T} e^{-\frac{E_A}{k_BT}}$$  \hspace{1cm} (2.4)

Where $\sigma_0$ is called pre-exponential factor and $E_A$ is called activation energy and plays a central role in ionic conductivity. The eq. 2.4 is known as Arrhenius equation which is also encountered in other area of physics and chemistry for ex. in chemical kinetics where the kinetic of many chemical reactions have been shown to have the same temperature dependence. In the intrinsic regime and/or in stoichiometric materials without any partial occupancy, $E_A$ is equal to
Figure 2.2 Variation of ionic conductivity as a function of dopant concentration. In general, the conductivity sharply increases, reaches a maximum and decreases as the dopant concentration increases.\textsuperscript{29}

$E_m + E_f/2$ while in the extrinsic regime or aliovalent-substituted compounds $E_A$ is equal to $E_m + E_t/2$ where $E_t$ is the trapping energy due to the interaction between defects and dopants. If $E_t$ is small compared to $E_m$ then it can be neglected and the activation energy is simply the migration barrier. However, it is important to keep in mind that in general, $E_A$ is simply an ‘apparent’ migration barrier as it also contains contribution from the defect formation energy or trapping energy. In practice, the ionic conductivity measurements are shown in the so-called Arrhenius plot where the logarithm of the product $\sigma T$ is plotted as a function of the inverse of the absolute temperature ($1/T$). If the ionic conductivity follows the Arrhenius equation, we will have a straight line whose slope is related to the activation energy $E_A$. Any curvature in the Arrhenius plots hint at a different diffusion mechanism for example the Vogel-Tamman-Fulcher mechanism\textsuperscript{32,33} which is commonly found in for the ionic conductivity in liquid and polymer system. The ionic
conductivity of several important classes of Li-ion conductors are shown in the Arrhenius plot in Figure 2.1 where straight line and curvature can be clearly discerned for solid-state crystalline Li-ion conductors (for ex. Li10GeP2S12) and liquid electrolytes (for ex. EC:DMC 1M LiPF6) as well as polymer electrolytes (such as Polyethylene oxide PEO-LiClO4). Increasing the concentration of mobile species such as vacancies or interstitial ions by aliovalent substitution is a very effective strategy to increase the ionic conductivity. However, there is several limitations with this approach. First of all, the concentration of aliovalent dopant which can be introduced into the lattice without phase separation can be quite small for some host structures limiting the amount of mobile species that can be created. For example, as can be seen from Figure 2.2, the fraction of Y2O3 which can be incorporated into ZrO2 to create oxygen vacancies is less than 30%. Second, compounds with aliovalent substitution tend to have lower stability compared to parent structure. Finally, it is commonly found that the conductivity often passes through a maximum and starts to decrease as more mobile species are added into the lattice as can be seen in Figure 2.2. This decrease in ionic conductivity is generally attributed to stronger interactions among the mobile species and the distortion of the host lattice trying to accommodate extra interstitial ions or vacancies into the lattice. Above a critical concentration of substitution, the distortion of the lattice is so strong that the increase in the migration energy surpasses the effect of increasing the concentration of mobile species and the ionic conductivity decreases. For instance, lithium-ion conductivity in Li3-xLa2/3-xTiO3 perovskites exhibits a dome shape as a function of lithium substitution, x. The lithium-ion conductivity becomes greater with increasing lithium concentration for x ≤ 0.12 (corresponding to an A-site vacancy concentration of ~10%) while a decrease in the conductivity is observed for higher lithium content. Due to the smaller ionic radius of Li+ (0.92 Å, with a coordination number of 8) compared to La3+ (1.36 Å, with a coordination number of 12), the large lithium-ion concentration induces local distortions, which slows down the diffusion and ion conduction. Similar observations are also noted for lithium-ion conduction in the NASICON structure such as Li1+xLa2/3-xTi2-x(PO4)3 and oxygen-ion conduction in the fluorite structure such as (1-x)ZrO2-(x)Y2O3 as shown in Figure 2.2. The detail understanding of the interaction between mobile ions and there to the local distortion is still lacking although progresses have been made especially from the molecular dynamic simulations. The coupling between mobile-ion concentration and lithium-ion mobility highlights challenges in using aliovalent substitution to greatly enhance the conductivity of lithium-ion conductors.
2.2 Solid-state Li-ion conductors

Solid-State Li-ions conductors is sub-class of inorganic materials which the ionic conductivity of lithium is appreciable. It covers a huge diversity of crystal structures (perovskite, garnet, Nasicon-like...) and chemistries (oxides, sulfides\textsuperscript{41,42}, nitrides\textsuperscript{43,44}, halides\textsuperscript{45-47}, hydrides\textsuperscript{48-51}...) as can be seen in Figure 2.1.\textsuperscript{29} Within each family, the ionic conductivity can span over many several orders of magnitudes but even more surprisingly is the fact that some of the best Li-ion conductors that have reported to date possess ionic conductivity comparable or even exceeding Li-ion conductivity in organic electrolytes EC:DMC 1M LiPF\textsubscript{6} used in commercial Li-ion batteries.\textsuperscript{26,26,52} These so-called superionic conductors (not to be confounded with superconductor) are characterized by presence of highly polarizable ions (S\textsuperscript{2-}, I\textsuperscript{-}...) and a complex distribution of Li-ions with numerous partial occupancy in the lattice.\textsuperscript{53} Traditionally, one effective way to
discover new Li-ion conductors is to do ion exchange on existing ionic conductor in which the mobile specie is not lithium. For instance, the Li argyrodite compounds are derived from the well-known silver argyrodite structure. Another example is the Nasicon-like family which is derived from the sodium conductor Nasicon family. Once a parent compound is discovered in new family of Lithium ion conductors, several strategies can be used to increase the ionic conductivity of that materials. One common strategy which was already alluded to in the previous section is to dope the parent structure with aliovalent dopant to create mobile charge carrier which can be interstitial ions or vacancies. This strategy has been widely and successfully used to increase the ion conductivity of several compounds. For example, in Figure 2.3, by partially substituting phosphorus by germanium in Li\textsubscript{3}PS\textsubscript{4}, the ionic conductivity can be increased by more than 3 orders of magnitude. Another strategy which aims at reducing the activation energy is to do isovalent substitution on the anions to introduce more polarizable ions into the lattice. For instance, by replacing oxygen by sulfur in Li\textsubscript{6}PO\textsubscript{5}Cl argyrodite, the Li-ion conductivity is hugely improved. While these strategies are very useful in optimizing the ionic conductivity within a family of known ionic conductors, it is of limited used when one tries to predict a new family of materials. Moreover, this huge variation ionic conductivity across that many chemistries and crystal structures pose a significant challenge in the its rationalization. In this chapter, we will give a detail overview of several descriptors that have been proposed in order to explain the trend in ionic conductivity or activation energy, but before diving into those details, we will first discuss the crystal structures of several commonly studied Li-ion conductors as we will see shortly, most of the descriptors are closely based on the crystal structure of the Li-ion conductors themselves.

2.2.1 Lisicon (Lithium superionic conductors)

Lisicon is one of the earliest and the most studied families of Li-ion conductors. Its parent compound, the so-called γ-Li\textsubscript{3}PO\textsubscript{4}, has an orthorhombic unit cell with space group $Pnma$. It is the high-temperature (HT) meta-stable phase of the compound. The low-temperature (LT) phase β-Li\textsubscript{3}PO\textsubscript{4} also has an orthorhombic unit cell but with $Pmn2_1$ space group. In both phases, the structure can be viewed as a distorted hexagonal close-packed oxygen sublattice in which the cations (for ex. Li\textsuperscript{+} and P\textsuperscript{5+}) occupy tetrahedral sites leaving all the octahedral sites empty (Figure 2.4). The difference between the low and high temperature phases resides in the occupancy of the tetrahedral interstices. In the LT phase, only one type of tetrahedral sites (T1
Figure 2.4 The crystal structure of the low and high temperature phases of Lisicon family. In the two phase, the structures can be viewed as distorted oxygen hexagonal sub-lattice. The difference resides in the occupancy of the tetrahedral interstices. In the LT phase, only T1 sites are occupied while in the HT phase, both T1 and T2 sites are occupied. All the octahedral sites are empty. LiO₄ tetrahedra form one dimensional chain of corner sharing units along the one of the crystallographic axes.

site) is occupied while in the HT phase, both T1 and T2 sites are occupied leading to some LiO₄ tetrahedrons pointing in opposite directions.⁶³⁶³ The LiO₄ and PO₄ tetrahedron form corner-sharing chain of tetrahedron between which Li-ions can diffuse.

2.2.2 Garnet family

Lithium conducting garnets are derived from the ideal garnet structure with the general formula A₃B₂(XO₄)₃ such as Ca₃Al₂(SiO₄)₃ (cubic unit cell and space group Ia3d, space group number 230).⁶⁴ A-sites are 8-fold coordinated (antiprismatic sites), B-sites are 6-fold coordinated (octahedral sites) and X-sites are 4-fold coordinated (tetrahedral sites) (Figure 2.5). In these materials, lithium ions occupy the tetrahedral positions as in Li₃Nd₃Te₂O₁₂.⁶⁵⁶⁵ However, more lithium can be added into the structure by changing the valence of the B and X cations leading to several stoichiometries of lithium-conducting garnets such as Li₃Ln₃Te₂O₁₂ (Ln = Y, Pr, Nd, Sm-
Figure 2.5 (a) The conventional unit cell of (cubic) garnet Li₅La₃Ta₂O₁₂ (space group Ia₃d). (b) Connectivity between various polyhedral units (LaO₈ antiprism, TaO₆ octahedra and LiO₄ tetrahedra) in the structure. (c) A section of 3-dimensional Li diffusion pathway through the lattice.⁶⁶

Lu), Li₅La₃M₂O₁₂ (M = Nb, Ta, Sb), Li₆Al₃M₂O₁₂ (A = Mg, Ca, Sr, Ba; M = Nb, Ta) and Li₇La₃M₂O₁₂ (M = Zr, Sn).⁶⁴,⁶⁶ Li₃Ln₃Te₂O₁₂ garnets, where lithium ions reside only in the tetrahedral sites, have low ionic conductivities. Replacing Te⁶⁺ by M⁵⁺ ions in the garnet structure introduces extra lithium ions leading to compositions such as Li₅La₃M₂O₁₂. The extra lithiums are distributed over the pseudo-octahedral sites (48g/96h sites) which are face-sharing with the
Figure 2.6 Crystal structure of Lithium conducting perovskite \( \text{Li}_{3x}\text{La}_{2/3-x}\text{Ti}_{1/3-2x}\text{TiO}_3 \). The Li distribution is very disordered but is believed to form alternating layers of Li-rich and Li-poor layers.

tetrahedral sites.\(^{67,68}\) Li diffusion is believed to occur between these tetrahedral and octahedral sites (Figure 2.5c). The exact Li occupancy of these sites is fairly complicated and is believed to be the determining factor for the activation energy in this family of Li-ion conductors.\(^{64,66}\)

### 2.2.3 Perovskite family

Li-conduction perovskite, with the general formula \( \text{Li}_{3x}\text{La}_{2/3-x}\text{Ti}_{1/3-2x}\text{TiO}_3\),\(^{37}\) is a highly defective perovskite which can be derived from ideal perovskite structure, with a general formula \( \text{ABO}_3 \) tuning the valence of the A-site and compensate the charge by introducing lithiums and vacancies. The ideal perovskite structure with a general formula \( \text{ABO}_3 \), cubic unit cell, and space group \( \text{Pm\bar{3}m} \) (space group number 221) consists of A-site ions (typically alkaline-earth or rare-earth elements) at the corners of a cube, B ions (typically transition metal ions) at the center and oxygen atoms at the face-center positions, where A sites are in 12-fold coordination and B sites are in 6-fold coordination \( \text{BO}_6 \) that share corners with each other. By changing the fraction of A-site cation, the concentration of Li and vacancy can be controlled and their interactions (that can lead to ordering of lithium/vacancies in the planes perpendicular to the c axis) can significantly influence ionic conductivity. The distribution of lithium in the lattice is fairly complex but it is
believed that at least for some concentration of mobile species (Li$^+$ and vacancies), lithiums form alternating Li-rich and Li-poor layers (Figure 2.6).\textsuperscript{69,70} Within these layers, lithium ions can diffuse by jumping in the $ab$ plane to an adjacent vacancy through a square planar bottleneck made of oxygen forming the corners of the octahedra. The size of this bottleneck can be varied by changing the B-site cation and has a very strong effect on the activation energy of Li conduction in these materials.\textsuperscript{71-73}

### 2.2.4 Nasicon-like family

The NASICON structure, crystallize in a rhombohedral unit cell with space group $R\bar{3}c$ (although monoclinic and orthorhombic phases have been reported)\textsuperscript{74,75} and with the general composition of LiM$_2$(XO$_4$)$_3$ where M is a tetravalent cation such Ti$^{4+}$, Ge$^{4+}$, Sn$^{4+}$, Hf$^{4+}$ or Zr$^{4+}$ and X can be P$^{5+}$ or As$^{5+}$.\textsuperscript{76-78} The structure is fairly open, consisting of isolated MO$_6$ octahedra interconnected via corner sharing PO$_4$ tetrahedra in alternating sequences (Figure 2.7a). Lithium
**Figure 2.8** a). The conventional unit cell of Argyrodite structure $\text{Li}_6\text{PS}_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br} \text{ or I}$) (space group $F\bar{4}3m$). b) Positions of Lithiums in the lattice as well as various possible jump sequences. When $\text{X} = \text{Cl}$ or Br, there is a disorder between the 4a and 4c sites which strongly affect the ionic conductivity. \(^{83}\)

Lithium can occupy two different sites in the structure: the M1 sites that are 6-fold coordinated (octahedral symmetry) ‘sandwiched’ between two MO₆ octahedra (Figure 2.7b), and the M2 sites that are 8-fold coordinated and located between two columns of MO₆ octahedra (Figure 2.7c).\(^{89}\) In the ‘stoichiometric’ compound i.e. with one Li per formula unit, only the M1 sites are occupied. Additional lithiums can be added to the structure by partial substituted $\text{M}^{4+}$ by $\text{M}'^{3+}$ leading to the general formula $\text{Li}_1+x\text{M}^{4+}_{2-x}\text{M}'^{3+}_x(\text{XO}_4)_3$.\(^{40,77,80}\) The extra Li ions reside in M2 site. Lithium diffusion occurs via hopping between these two sites by passing through the triangular faces formed by oxygen ions which constitute the bottleneck in the structure (Figure 2.7c). Partial occupancies of lithium ions on those two sites is crucial for fast lithium-ion conduction, especially as vacancies are required at the intersection of the conduction pathways to give access to three-dimensional diffusion within the structure.\(^{81}\) As in the perovskite structure, the size of the bottleneck is of paramount importance and can be varied by changing the ratio of the tetravalent cations on the M sites.

### 2.2.5 Argyrodite family

Lithium argyrodite $\text{Li}_6\text{PS}_5\text{X}$ (with $\text{X} = \text{Cl}, \text{Br}$ or I) is a newly discovered family of Li-ions conductors which isostructural to the Cu- and Ag-argyrodite compounds.\(^{54,55,82}\) These materials
crystallize into a structure based on tetrahedral close packing of anions (cubic unit cell with space group \( F\overline{4}3m \), space group number 216).\(^5^4,^5^4,^8^3 \) The halide anions form a face-centered cubic (FCC) lattice which is inter-penetrated by another FCC lattice of PS\(_4\) tetrahedron. Within this close packed structure, phosphorus atoms fill tetrahedral interstices, forming a network of isolated PS\(_4\) tetrahedron (similarly to the thio-LISICON structure), while lithium ions are randomly distributed over the remaining tetrahedral interstices (48h and 24g sites) forming cage-like structure (Figure 2.8).\(^8^3,^8^4 \) Several jump sequences are possible in this structure but long-range diffusion is believed to be mediated by the inter-cage jumps.\(^8^3,^8^5 \) Lithium-ion diffusion occurs through these partially occupied positions forming hexagonal cages, which are connected to each other by an interstitial site around the halide/sulfur ions in the case of Li\(_6\)PS\(_5\)Cl and around the sulfur anions in Li\(_6\)PS\(_5\)I. The difference in the connectivity of the hexagonal cages and the distribution of lithium among the different sites as well as the disorder on the S\(^2^-/X^-\) sublattice which exist in chloride and bromide, but not in iodide, may explain why Li\(_6\)PS\(_5\)I has significantly lower ionic conductivity compare to Li\(_6\)PS\(_5\)Cl and Li\(_6\)PS\(_5\)Br.\(^8^5,^8^6 \)

### 2.3 Crystal-structure based descriptor for activation energy.

#### 2.3.1 Volume of the unit cell

One of the simplest and the most widely used descriptor to explain the variation of activation energy within some families of Li-ion conductors. For instance, the activation energy for Li in Lisicon Li\(_{3.5}\)M\(_{0.5}\)M'\(_{0.5}\)O\(_4\) (M is tetravalent cation such Si, Ge and Ti, M' is pentavalent cation such as P, As and V) decreases with the volume of the unit cell (normalized to the number of Li in the unit cell) accompanied by an increase in the ionic conductivity (Figure 2.9a).\(^5^7,^5^9,^6^0,^8^7 \) Similarly, the activation energy in Nasicon-like compounds LiM\(_x\)M'\(_{2-x}\)(PO\(_4\))\(_3\) (M = Ti and M' = Ge, Zr or Hf) also decrease with the volume of the unit cell per Li ion (Figure 2.9b) as we substitute the M and M' site by cation with larger ionic radius.\(^8^1,^8^8 \) The increase in the unit cell volume of Nasicon-like structures also accompanies an increase in the bottleneck size in the structure (Figure 2.9d), leading to a significant drop in the activation energy and an increase by more than two orders of magnitude in ionic conductivity. Interestingly, while the bottleneck size increases monotonously with the larger size of substituted ion, the activation energy seems to plateau once the size of the bottleneck reaches \(~2.05\) Å suggesting that there might be an optimal size of the bottleneck (not too large nor too small) for which the activation energy is minimal.\(^8^1 \)
Figure 2.9 Correlation between ionic conductivity and activation with the lattice volume (normalized by the number of Li in the unit cell) in a) Lisicon, b) Nasicon-like structure. c) Correlation between ionic conductivity and Li content as well as site occupancy (tetrahedral vs octahedral) in Garnet structure. d) Correlation between the activation energy and the size of the bottleneck in Nasicon-like materials. Adapted from ref. 29

For Garnet, the variation in ionic conductivity has been rationalized in terms of the occupancy of various Li sites in the garnet structure (tetrahedral sites 24d and (pseudo)octahedral sites 48g/96h). The lowest concentration of Li in the garnet structure is 3 Li per formula unit (fu). At this concentration, all Li ions occupy the tetrahedral sites, leaving all the octahedral sites empty (Figure 2.9c). While more and more lithums are stuffed into the lattice (up to 7 Li per fu), those extra lithums primarily go into the octahedral sites but interestingly the occupancy of the tetrahedral sites decreases slightly indicating that the presence of Li at 48g/96h sites somehow destabilizes some lithums which are located at the 24d sites. Because the ionic conductivity is very low when all Lithums are in tetrahedral sites and increases with the increasing occupancy of...
the octahedral sites, it is suggested that only Li in 48g/96h are mobile and contribute to the long-range diffusion in the garnet structure.65-67

2.3.1 Mechanical strain

Since the volume of the unit cell can affect the ionic conductivity and activation energy of Lithium motion, we must be able to tune this quantity by applying mechanical strain that can modify the lattice parameters of the materials. This is indeed what researcher have been able to prove, albeit computationally, by applying (hydrostatic) tensile/compressive strain on the Li10GeP2S12 (LGPS)89 and cubic-Li7La3Zr2O12 (c-LLZO)90. The calculations were done using ab-initio molecular dynamics (AIMD) with density functional theory (DFT). As expected, a compressive lead to an increase in activation energy and a decrease in ionic conductivity due to a reduction in the volume of the unit cell while an applied tensile strain lead to a decrease of activation energy and correspondingly and increase in ionic conductivity (Figure 2.10a).29,89,90 It is interesting, however, to note that the effect of compressive and tensile strain is not ‘symmetric’ namely a compressive strain leads to a much more drastic increase of activation energy while a similar level of tensile strain only moderately decreases the activation energy suggesting that in the already very good Li-ion conductors (LGPS and c-LLZO) the diffusion channel size is already close to the optimum, a phenomena similar the variation of the activation energy with the bottleneck size seen in Nasicon-like family.

The experimental realization of these strain-dependent ionic conductivity/activation energy for Li-ion conductors is still lacking probably due to the difficulty to deposit these complex materials epitaxially on suitable substrates that generate appreciable level of strain on the Li-conducting materials.91 However, this line of thinking has been extensively applied to the studied of oxygen ion O2- conductors especially Ytria-Stabilized Zirconia (YSZ) and the effects of applied strain via epitaxy on the mobility of O2- are well documented.92-97 In Figure 2.10b, the activation energy of O2- diffusion in heterostructures of YSZ sandwiched between different ‘spacer’ materials (Sc2O3, Y2O3 and Al2O3)92-94 was measured as a function of layer thickness. Depending the lattice mismatch between YSZ and the spacer materials, different level of compressive or tensile strain can be imposed on the YSZ which were ‘epitaxially’ grown on the spacer materials. For a give layer thickness, we can see that a negative a lattice mismatch (meaning that the lattice constant of
Figure 2.10 a) Variation of the (computed) activation energy and ionic conductivity of Li$_{10}$GeP$_2$S$_{12}$ and cubic-Li$_7$La$_3$Zr$_2$O$_{12}$ garnet as a function of applied strain. b) Variation of activation energy of O$^{2-}$ diffusion in YSZ heterostructure as a function of layer thickness. c) Variation of (computed) activation energy of O$^{2-}$ diffusion in YSZ epitaxially ‘growth’ on different substrates.$^{29}$

the spacer is smaller than YSZ) or equivalently a compressive strain lead to an increase in activation energy compared to un-strained or bulk YSZ (shown as the gray horizontal bar in Figure
2.1 Ob) as one expects. In contrast, a positive lattice mismatch (tensile strain) such as in YSZ|Y₂O₃ or YSZ|Al₂O₃ heterostructures leads to decrease in activation energy compared to bulk YSZ. As we increase the layer thickness, the strain on YSZ layers becomes smaller and smaller due to the partial lattice relaxation (via creation of dislocations for example). As a result, the activation energy of YSZ heterostructures converges to the bulk value as expected. Notice that the values of lattice mismatch on Figure 2.10b are nominal values and the actual strain on YSZ is likely to be smaller than these nominal values, as the large lattice mismatch between the spacer materials and YSZ might lead to the partial lattice relaxation even for thin layers. There are also several computational studies that confirmed these experimental observations.⁹⁸⁻¹⁰⁰ Figure 2.10c shows the computed activation from AIMD of YSZ epitaxially grown on different substrates (Al₂O₃, SrTiO₃ (STO) and KTaO₃ (KTO)) with different level of lattice mismatch. We can see very clearly that as the tensile strain increases (larger positive lattice mismatch) the activation energy of O²⁻ decreases drastically compared to bulk YSZ, in perfect agreement with the experiments. Notice that the effect of strain or lattice mismatch is more pronounced since computationally, we can impose a level of strain which exactly the same as the nominal value with lattice relaxation that reduce the actual level of strain that can be imposed on the ion-conducting materials in an epitaxial heterostructure. Caution should be taken when assessing ion-conductivity changes of these thin-film studies. First, thin films grown on different substrates can greatly vary from study to study. For example, no change is observed for oxygen-ion conductivity for YSZ thin films (30-300 nm) grown on MgO, Al₂O₃ or SrTiO₃⁹⁷ single-crystal substrate and YSZ/CeO₂ multilayers. Second, other factors besides strain, such as changes in the nature of metal-oxygen bonds between oxygen sub-lattices at the interface,⁹⁸ mobile ion concentration¹⁰¹ and new phases created at the interface⁹⁸ should also be considered.

2.3.2 Volume of diffusion pathway

A more refined structural descriptor that has been proposed to correlate with the ionic conductivity/activation energy is related to the volume of diffusion which can be viewed as the ‘free volume’ accessible to the mobile specie while exclude the volume associated with the anions the other non-mobile ions. One simple and intuitive way to determine this diffusion pathway volume was proposed by Adam and Swenson¹⁰²⁻¹⁰⁴ based on the bond valence method developed
Figure 2.11  a) One example of diffusion pathway as determined from the bond valence method in Lithium argyrodite Li₆PS₅Cl at various values of the bond valence mismatch threshold. b) Correlation between the fraction of diffusion pathway (multiplied by square root of the mass of diffusion specie) and the activation energy and the ionic conductivity in Ag⁺, Li⁺ and Na⁺ conducting glasses.²⁹

by Brown.¹⁰⁵ The main concept in the bond valence method is the notion of the 'valence' of a chemical bond between the atom i and j, \( s_{i-j} \), which can be calculated using the formula:¹⁰⁵

\[
s_{i-j} = \exp \left( \frac{R_o - R}{b} \right)
\]

where R is the bond length and \( R_o \) and b can be considered, to a good approximation, as constants that don’t depend on the crystal structure being considered. The bond valence method has been used quite extensively in crystallography in combination with diffraction to help refinement of crystal structures of new compounds. It has been found empirically that if a crystal is stable, the bond valence sum of each atom \( i, V_i = \sum_j s_{i-j} \), where j runs over all nearest neighbors, will be very close to the formal charge of that atom.¹⁰⁵ To determine the diffusion pathway, the unit cell is divided into a fine 3D grid. At each node of this grid, the bond valence sum of the diffusing species is calculated. The key idea in Adam and Swensen method is to define the diffusion pathway in crystalline and amorphous solids as the percolating region, where the bond valence mismatch of the mobile species, defined as the difference between the bond valence sum and the formal charge, is below a certain threshold. The value of this threshold can significantly influence the volume and the topology of the diffusion pathway in a given structure.¹⁰²,¹⁰³ If the threshold is too
small then there will be no percolating diffusion pathway but only disconnected regions as can be
seen in magenta in Figure 2.11a in the case of Li₆PS₅Cl.⁸⁶ On the contrary, if the threshold is too
large, then the entire unit cell will become part of the diffusion pathway, a situation obviously non-
physical. Therefore, the value of this threshold must be carefully chosen and ideally independent
of the structure and chemistry of the material being considered. Unfortunately, there is no unique
way to determine the value of this critical parameter. One possibility is to choose the lowest value
of the bond valence mismatch at which a percolating pathway starts to appear (which is shown in
cyan in Figure 2.11a). However, for the purpose of comparing the volume of diffusion pathway
between different compounds, it makes more sense to choose a fixed value of bond valence
mismatch and compare the diffusion pathway volume at that value of bond valence mismatch. A
fixed value of the bond valence mismatch of 0.2 has also been used to determine the diffusion
pathway in Li⁺, Na⁺, K⁺, Ag⁺ and Cu⁺ conductors.¹⁰⁶
A very good correlation has been found between the ionic conductivity as well as the activation
energy of diffusion in silver-, sodium-, and lithium-ion-conducting glasses with the fractional
volume of diffusion pathway (F) (multiplied by the square root of the mass of the mobile species)
as shown in Figure 2.11b.¹⁰²,¹⁰³,¹⁰⁷ The fractional volume of diffusion pathway (F) is defined as
the ratio between the volume of diffusion pathway and the volume of the unit cell, as shown in
Figure 2.9b. The activation energy (the ionic conductivity) decreases (increases) as the fractional
volume (F) increases. This descriptor has been used in a high-throughput calculation to find
possible candidates of lithium-, sodium-, potassium-, silver and copper- ion conductors having
potentially higher ionic conductivity. This method has also been used to study crystalline lithium-
ion conductors and electrodes, and by varying the threshold of the bond valence mismatch,
researchers can get information not only about the diffusion pathways¹⁰⁸ but also the fraction of
mobile lithium contributing to conduction as well as possible diffusion mechanisms that are
dominant in these materials.¹⁰³ Another interesting development of this idea of bond valence
method is the construction of empirical potential that can be used in classical molecular dynamics
to study diffusion process.¹⁰⁹
Figure 2.12 a) The increase of ionic conductivity across 3 different series of Li-ion conductors as the anions become more polarizable. b) Correlation between ionic conductivity in Lithium halides family as a function of the polarizability of the halide, Li-halide bond distance and the electronegativity. 29

2.4 Polarizability of the anion sublattice

It is well-known that the polarizability of elements or ions increases as we move down the periodic table (for ex. from oxygen to sulfur to selenide in chalcogens or from fluorine to iodine in halogens). This trend can be put in perspective with an interesting fact that when changing the ligand by moving down in the periodic table, the ionic conductivity of cations typically increases. This trend is clearly shown in Figure 2.12a when changing the ligand from F to I, Ag+ and Li+ conductivity increases by many orders of magnitude in halides LiX (X = F, Cl, Br and I)110 and the olivine Li2ZnM4 (M = Cl, Br and I)111-113. Several equivalent explanations have been proposed to explain this behavior. First, large polarizable ions tend to be ‘softer’ the small less polarizable ions, allowing the mobile specie to ‘squeeze’ through their electronic cloud more easily with lower activation energy. It can also be argued that as we move down the periodic table, the ionic size increases while the formal charge remains constant. As a result, the charge density on the anion is smaller for more polarizable (larger) ions leading to smaller electrostatic interaction with the mobile specie especially at the saddle point and hence a smaller activation energy. The increasing lithium-ion conductivity in halides from LiF to LiI can be correlated with increasing Li-X distance, halogen atom polarizability and reduced electronegativity of the halogen atom, as shown in Figure 2.12b. Interestingly, the ionic conductivity of the lithium ion in the argyrodites family seems to
Figure 2.13 Correlation between the activation energy of ionic conductors with a) high-frequency dielectric constant $\varepsilon_\infty$ and b) low-energy phonon frequency $\omega_{LEO}$.\textsuperscript{29}

Contradict this trend as the conductivity of Li\textsubscript{6}PS\textsubscript{5}I is the lowest in the series while according to this trend we expect it to be the highest (Figure 2.3). The reason for this apparent contradiction is the fact that in this family, the dominant anions are S\textsuperscript{2-} which outnumber the halide anions by a ratio 5 to 1 per formula unit. Therefore, we expect that the halide anions have a much smaller effect on ionic conductivity/activation energy compared to S\textsuperscript{2-} anions. Indeed, the conductivity of Li\textsubscript{6}PO\textsubscript{5}Cl is several orders of magnitudes lower than its sulfur-containing counterpart (see Figure 2.3). Moreover, in the case of Li\textsubscript{6}PS\textsubscript{5}I, it was found that S\textsuperscript{2-} and I\textsuperscript{-} anions order into well separate positions in the lattice unlike in Li\textsubscript{6}PS\textsubscript{5}Cl and Li\textsubscript{6}PS\textsubscript{5}Br where there is a substantial disordering between S\textsuperscript{2-} and halide sites.

Also apparent from Figure 2.3, the substitution of oxygen by sulfur in the $\gamma$-Li\textsubscript{3}PO\textsubscript{4} type structure to form thio-LISICON leads to an increase of several orders of magnitude in the lithium-ion conductivity.\textsuperscript{114-116} This trend can also be found in computational studies where, upon substitution of O by S phosphate compounds such as Li\textsubscript{7}P\textsubscript{3}O\textsubscript{11} and Li\textsubscript{7}P\textsubscript{3}S\textsubscript{11} or Li\textsubscript{4}P\textsubscript{2}O\textsubscript{7} and Li\textsubscript{4}P\textsubscript{2}S\textsubscript{7}, the activation energy significantly decreases.\textsuperscript{117} Similar trends in enhanced lithium-ion mobility (reduced activation energy) have been found computationally for the Li\textsubscript{10}GeP\textsubscript{2}X\textsubscript{12} (X = O, S, or Se) family going from O to S or Se.\textsuperscript{89} Again, this trend is in agreement with the concept shown in Figure 12b as S\textsuperscript{2-} and Se\textsuperscript{2-} are larger and have a higher polarizability than O\textsuperscript{2-}, confirming this approach as an effective strategy to increase ionic conductivity in solid-state lithium-ion.
conductors and may potentially be also applicable to other ion conducting materials such as Na\(^+\) or Mg\(^{2+}\) ion conductors.

### 2.5 Lattice dynamics

The correlation between polarizability and activation energy discussed in the previous section suggests that other correlations might also exist as the polarizability can be related to many different physical parameters. For example, the well-known Clausius-Mossotti relation relates the polarizability \(\alpha\) to the high-frequency dielectric constant \(\varepsilon_\infty\) as (in the case of cubic binary compounds)\(^{118}\):

\[
\varepsilon_\infty - 1 = \frac{4\pi\alpha}{\varepsilon_\infty + 2}
\]

Where \(V_a\) is the volume of the primitive cell. Indeed, such correlation has been found by Wakamura between the activation energy and the high-frequency dielectric constant \(\varepsilon_\infty\) of Ag\(^+\), F\(^-\), Li\(^+\) and a few Na\(^+\), Cu\(^+\) as well as Cl\(^-\) conductors shown in Figure 2.13a.\(^{119}\) The activation energy decreases with decreasing high-frequency dielectric constant \(\varepsilon_\infty\) as expected since \(\varepsilon_\infty\) increases with polarizability.

The correlation between activation energy with \(\varepsilon_\infty\) also hints at another correlation with phonon frequency in particular, with the frequency of the transverse optical phonon \(\omega_{TO}\) which can be related to \(\varepsilon_\infty\) using the Lyddane-Sachs-Teller relation:\(^{120}\)

\[
\frac{\omega_{TO}^2}{\omega_{LO}^2} = \frac{\varepsilon_\infty}{\varepsilon_o}
\]

Where \(\omega_{LO}\) is the frequency of the longitudinal optical mode and \(\varepsilon_o\) is the static dielectric constant. As expected, a correlation between the activation energy and \(\omega_{TO}\) (equivalent to \(\omega_{LEO}\), frequency of the low-energy optical mode) has been found as shown in Figure 2.13b.\(^{121}\) The activation energy decreases with decreasing \(\omega_{TO}\) in agreement with the idea that low phonon frequency is associated with large vibration amplitude, hence increasing the probability of the mobile species to hop to the neighboring lattice site. It is interesting to note that the correlation between activation energy and lattice dynamics also exists for other material systems. For instance, it was found that the enthalpy of self-diffusion (normalized by the melting point) correlates with the frequency of longitudinal acoustic phonon at 2/3 \((111)\) in the Brillouin zone in body-centered cubic metals such alkaline and some transition metals.\(^{122}\) Moreover, computational studies reveal that the computed enthalpy
of migration of interstitial $\text{O}^{2-}$ in Ruddlesden-Popper series decreases with the force constant associated with the rotation of octahedron in the lattice.$^{123}$ One of the main objective of this thesis is to extend and deepen the understanding of the physical origins underlying this type of correlation to Li-ion conductors. The results will be present in detail in the next chapter.
Chapter 3

Influence of Lattice Dynamics on Ionic Conductivity and Stability in Solid-State Lithium Conductors

As we alluded to in the last part of the previous chapter, the correlations between lattice dynamics and activation energy or mobility in ionic conductors have been reported in many systems. In particular, we have mentioned the work of Wakamura\textsuperscript{119,121} where he has shown that the activation energy correlates with the 'low-energy' phonon frequency and the high-frequency dielectric constant. However, it is worthwhile to note no relevant Li-ion conductors were included in his original work as can be seen from the Figure 2.13. Moreover, the correlation he proposed covers many different type of ionic conductors (Ag\textsuperscript{+}, O\textsuperscript{2-}, F\textsuperscript{-}...) and yet the number of compounds included in that study is very small compared to the number of known ionic conductors at the time which raises the possibility that the correlation might not be very strong or even non-existent when more compounds are included. Finally, the nature of the ‘low-energy’ phonon was not very clearly defined which makes it difficult to measure or compute this frequency. In this chapter, we explore more in depth this correlation by focusing specifically on a few family of Li-ion conductors and by proposing a new descriptor based on phonon frequency which are rigorously defined. Finally, we extend this idea to account for the stability of these Li-ion conductors thereby providing the rationalization of the mobility and stability on the same footing.

3.1 Intuitive understanding of the relationship between lattice dynamics and migration barrier

To understand the relationship between lattice dynamics and migration barrier, we proposed a simple and intuitive idea illustrated in Figure 3.1. The figure depicts the energy
Figure 3.1 Schematic of the energy landscape as ‘felt’ by Li-ions (red circle) in solid electrolytes. In materials with high migration barrier $E_m$ (the bottom graph), Li-ion vibrate around its equilibrium position with small displacement amplitude $u$. In contrast, in materials with low $E_m$ (the top graph), Li-ion move further away from its equilibrium position with larger $u$.\textsuperscript{159}

landscape as experienced by Li-ions in the lattice. In materials with high migration barriers, we can envision that Li-ions will vibrate back and forth close to their equilibrium position with low probability to jump the neighboring sites (bottom curve). In contrast, in materials the low migration barriers, i.e. relatively flat energy landscape, Li-ions will oscillate around their equilibrium position with larger displacement amplitude and correspondingly a higher probability to over the barrier to the adjacent sites. From this simple consideration, we expect that there is relationship between the displacement amplitude $u$ and the migration barrier $E_m$. On the other hand, if we assume the Einstein model of solid, namely by assuming that each oscillator vibrates independently from one another, one can show that the square of the displacement amplitude is inversely proportional to the square of Einstein frequency $\omega_E^{120}$:

$$\langle |u|^2 \rangle = \frac{3k_BT}{m\omega_E^2}$$

(3.1)

Where $k_B$, $T$ and $m$ denote respectively the Boltzmann constant, the temperature and the mass of the ion forming the lattice. By combining these two arguments, we can hypothesize that a correlation might exist between the vibration frequency (modelled as Einstein frequency) and the migration barrier. As we will show in the following sections, this correlation does indeed exist. It is also very interesting to note that, using a much more rigorous theoretical model of superionic
conductors, Rice and Roth arrived at very similar conclusion regarding the relationship between the jump frequency \( v_o \) and activation energy \( E_a \):

\[
v_o = \frac{1}{a_o} \sqrt{\frac{2E_a}{m}}
\]

(3.2)

Where \( a_o \) and \( m \) are respectively the jump distance and the mass of the mobile specie.

### 3.2 Lisicon and olivine as model systems

In order to explore in-depth the correlation between the migration barrier and lattice dynamics in Li-ion conductors, we focus on two families of well-known Li-ion conductors namely Lisicon and Olivine. Li-ion conductivity in Lisicon have been studied in great detail especially by Anthony West in the 80s and 90s while Olivine structure is a well-known family of cathode materials in particular lithium iron phosphate LiFePO₄. Another reason why we choose these two families is the similarity of their structures. While not evidence from Figure 3.2, a close examination reveals that these two structures both have a (distorted) hexagonal close packed (HCP) lattice of anions (mainly oxygen and sulfur). The main difference resides in the occupancy of tetrahedral and octahedral sites by Li ions. In ideal HCP lattice, there are two non-equivalent tetrahedral sites typically denoted as T1 and T2. These two sites aren’t never simultaneously occupied due to their common face sharing configuration leading to a very close proximity between the two ions in these sites. Each type of type of tetrahedron are connect via their corners forming one-dimension chains along a crystallographic axis. The remaining ‘void’ in the lattice are filled with the octahedral sites which also form 1-D chains of the edge-sharing octahedra (Figure 3.2). In the LT phase of Lisicon (space group \( Pmn21 \)), only T1 sites are occupied by Li and non-Li cations while in the HT phase (space group \( Pnma \)), some cations move out of the T1 sites to T2 sites leading to configuration in which LiO₄ tetrahedra point in opposite directions. In Lisicon, all octahedral sites are empty. This is in contrast with the Olivine compounds in which all Lithiums are in octahedral environments (Figure 3.2). By keeping the anion framework the same across different compounds, we can make a systematic study of the properties of interest and yet avoid ‘trivial’ correlations by allowing the local coordination of Lithium ions to be different (tetrahedral in Lisicon vs octahedral in Olivine). Another important reasons which let us to focus on these families is the flexibility of their lattice which can accommodate different cations and
Figure 3.2 The first column represent the ideal HCP structure with all the interstices within it. There two non-equivalent tetrahedral sites T1 and T2 that are face sharing. Each type of tetrahedral sites is connected with each other to form 1-D chain of corner shared tetrahedra. The octahedral sites form also 1D-chain of edge sharing octahedron. The middle column shows the HT and LT phase of Lisicon and Olivine structures. In Lisicon, all lithiums occupy tetrahedral sites while in Olivine, Li occupies octahedral sites.\textsuperscript{159}

anions on various sites therefore enabling a rich chemical space to be explored. This is illustrated in Figure 3.3 for Lisicon. Starting from the parent compounds $\gamma$-Li$_3$PO$_4$, one can do aliovalent substitution on the cation sites leading to compounds such as Li$_3$VO$_4$\textsuperscript{59} and Li$_3$AsO$_4$\textsuperscript{60} which also
Figure 3.3 Different substitution schemes that can be applied to the Lisicon $\gamma$-Li$_3$PO$_4$ without significantly changing its structure. This flexibility enables a rich chemical space to be explored and constitutes one of the main reasons to choose this family of compounds as our model system.

...have similar structures in both HT and LT phases. We can also do isovalent substitution on the anion sites by replacing oxygens by sulfurs, giving rise to the thio-Lisicon compounds which have much higher ionic conductivity than the oxides. Similarly, one can also do aliovalent substitutions on the cation and anions sites to create extra mobile charge carriers which can also greatly influence the ionic conductivity. For instance, by (partially) replacing P$^{5+}$ by Ge$^{4+}$, additional Li$^+$ have to be incorporated into the lattice to maintain charge neutrality. The ionic conductivity of resulting compounds, Li$_{3+x}$Ge$_x$P$_{1-x}$O$_4$ is many orders of magnitude higher than the stoichiometric Li$_3$PO$_4$. Aliovalent substitutions on the anion have also been attempted although it is much more difficult to obtain a crystalline phase. For example, a partial substitution of oxygen by nitrogen leads to the well-known Li-ion conductor oxynitride LiPON which is amorphous. Crystalline can be obtained under very narrow range of concentration of nitrogen.

Table 3.1 lists all the compounds that we include in this study which include all the stoichiometric compositions of LISICON and Olivine without transition metal ions in the Inorganic Crystal Structure Database (ICSD). Some olivines such as LiCdPO$_4$, LiScGeO$_4$ and LiTmSiO$_4$ were...
Table 3.1 List of all compounds in Lisicon and Olivine families included in this study. The Li_{10}GeP_2S_{12}-like compounds are also included although their structures are different since chemically they are very similar to thio-Lisicon. The color code is explained in the text.\textsuperscript{159}

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Crystal structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lisicon Pnma</td>
<td>Li_3VO_4, Li_3PO_4, Li_3AsO_4, Li_3PS_4, Li_4GeS_4, Li_4SnS_4, Li_2CdSiO_4, Li_2MgGeO_4, Li_{3.4}Ge_{0.4}P_{0.6}O_4, Li_{3.25}Ge_{0.25}P_{0.75}S_4 and Li_{3+x}Ge_xV_{1-x}O_4 (x = 0.2, 0.4, 0.6, 0.8 and 1)</td>
</tr>
<tr>
<td>Lisicon Pmn2_1</td>
<td>Li_3VO_4, Li_3PO_4, Li_3AsO_4, Li_3PS_4, Li_2CdGeO_4, Li_2CdGeS_4, Li_2CdGeSe_4, Li_2CdSiS_4 and Li_2CdSnS_4</td>
</tr>
<tr>
<td>Li_{10}GeP_2S_{12}-like P4_2/nmc</td>
<td>Li_{3.4}Ge_{0.4}P_{0.6}S_4 and Li_{10}SnP_2S_{12}</td>
</tr>
<tr>
<td>Olivine Pnma</td>
<td>LiMgPO_4, LiMgAsO_4, LiMgVO_4, LiScSiO_4, LiInGeO_4, LiInSiO_4</td>
</tr>
</tbody>
</table>

also considered by not include in this table due to the presence of imaginary frequency in the computed phonon DOS which suggests that those compounds are not stable at 0K. Total phonon densities of states (DOS) of some select LISICON compounds including Li_4GeO_4 (Cmcm), Li_3AsO_4 (Pnma), Li_3PO_4 (Pmn2_1), Li_3PS_4 (Pnma), Li_4SnS_4 (Pnma), Li_{3.6}Ge_{0.6}V_{0.4}O_4 (Pnma), Li_{3.33}Sn_{0.33}P_{0.67}S_{4} (P4_2/nmc) and Li_{3.4}Ge_{0.4}P_{0.6}S_4 (P4_2/nmc) were measured with inelastic neutron scattering (INS) for the first time. The computed total as well as atom-projected phonon DOS of all the stoichiometric compounds in LISICON (both Pnma and Pmn2_1) and Olivine can be found in Appendix E. Compounds whose lithium conductivity was measured in this work (Li_3PO_4 (Pnma...
and Pmn2₁), Li₃VO₄ (Pmn2₁) LiMgPO₄ (Pnma), Li₃.₄Ge₀.₄P₀.₆O₄ (Pnma), Li₃.₄Ge₀.₄P₀.₆S₄ (P4₂/nmc) and Li₃₊ₓGeₓV₁₋ₓO₄, where x = 0.2, 0.4, 0.6, 0.8 and 1) or prior work (Li₃PO₄ (Pnma), LiMgPO₄ (Pnma), Li₃VO₄ (Pmn2₁), Li₃₊ₓGeₓV₁₋ₓO₄ (Pnma, x = 0.2, 0.4, 0.6 and 0.8), Li₃AsO₄ (Pnma), Li₃PS₄ Pnm2₁ and Pnma, Li₄GeS₄, Li₄SnS₄, and Li₃.₃Sn₀.₃P₀.₇S₄) and phonon DOS measured in this work are shown in green, compounds which are known in the ICSD but neither ionic conductivity nor phonon DOS were measured are shown in black, and finally structures that were computed only to complete the compositional series with known experimental data are shown in orange. For example, Li₂CdGeSe₄ were added to complete the anion substitution series of Li₂CdGeO₄ and Li₂CdGeS₄ known in the ICSD, Li₂CdSiS₄ were added to complete the cation substitution series of Li₂CdGeS₄ and Li₂CdSnS₄ known in the ICSD. LiMgVO₄ exists but has a different structure from Olivine. We include Olivine LiMgVO₄ that was computed only to compare with LiMgPO₄, which can be compared with parallel LISICON compounds of Li₃PO₄ and Li₃VO₄.

### 3.3 Variation of Phonon Density of States (DOS) with temperature, chemical substitution and concentration of mobile specie

Before making any quantitative assessment of the correlation between lattice dynamics and activation energy or migration barrier, we first make some qualitative observations that lends support to our hypothesis. One of these observations, shown in Figure 2.4 are based on the phonon DOS of Lisicon. In each panel, the top graph is the phonon DOS measured by inelastic neutron scattering (INS) with time-of-flight spectroscopy and the bottom graph is the (neutron-weighted) computed phonon DOS using Density functional theory (DFT) with the finite displacement method. The shades area corresponds to the projection of the total phonon DOS on the Li sublattice and give the contribution of Li-ions vibration to the total DOS. Details of INS measurements, data analysis and extractions, DFT computation along with parameters and convergence test are given in appendix A and B. Cation and anion substitutions in the Li₃PO₄ structural family were shown to induce systematic changes by examining measured phonon DOS. The measured and computed phonon DOS of Li₃PO₄ (Pnma), Li₃PS₄ (Pnm2₁), Li₃.₄Ge₀.₄P₀.₆O₄ (Pnma) and Li₃.₂₅Ge₀.₂₅P₀.₇₅S₄ (Pnma) are shown as example in Figure 3.4a-d. Measured phonon DOS of other LISICON(-like) and Olivine LiMgPO₄ compounds can be found in appendix B. As can be seen from Figure 2.4, the agreement between the measured phonon DOS (at 100 K) and the computed phonon DOS are pretty remarkable especially for stoichiometric compounds. The main
Experimental phonon DOS collected at 100 K are shown on top while computed phonon DC 0 K on the bottom as well as the computed lithium-projected DOS (shaded). (a) Li$_3$PO$_4$ (Pnma) (b) Li$_3$PS$_4$ (Pmn2$_1$) (c) Li$_3$Ge$_{0.4}$P$_{0.6}$O$_4$ (Pnma) and (d) Li$_3$Ge$_{0.25}$P$_{0.75}$S$_4$ (Pnma).$^{159}$

discrepancy is a slight red-shift of the high-energy mode in the computation which a well-documented issue with the PBE functional used for these calculations.$^{129}$ One of the most striking change is the softening of phonon modes in Li$_3$PO$_4$ (Pnma) upon substitution of oxygen by sulfur (Figure 3.4a and 3.4b). The cut-off frequency in Li$_3$PO$_4$ (Pnma) is $\sim$140 meV compared to $\sim$80 meV for Li$_3$PS$_4$ (Pmn2$_1$). This softening of phonon is to put in perspective with the reduction in the activation energy from $\sim$1.2 eV in Li$_3$PO$_4$ (Pnma) to $\sim$0.6 eV in Li$_3$PS$_4$ (Pmn2$_1$). Similar observation can also be made for the Ge substituted Li$_{3.4}$Ge$_{0.4}$P$_{0.6}$O$_4$ (Pnma) in Figure 3.4c and Li$_{3.4}$Ge$_{0.4}$P$_{0.6}$S$_4$ (Pnma) in Figure 3.4d. In contrast, isovalent substitution of the cation produce a much less drastic change in the phonon DOS as can be seen in Figure 3.5a and 3.5b for Li$_3$VO$_4$. 


and b) Li$_4$GeS$_4$. Isovalent substitution of cation have little influence on the phonon DOS.\textsuperscript{159}

and Li$_4$GeSe$_4$ which is consistent the fact that isovalent substitution of cation doesn’t affect the activation energy in Li-ion conductors in significant way. Similar lattice softening was found for other sulfides relative to oxides as shown by the computed phonon DOS in appendix E. Also shown along the total (computed) phonon DOS are the projected DOS on different sublattices which make up the structure. Generally speaking, the high-energy part of the DOS originates from the vibrations of the polyhedral units such as PO$_4$ or PS$_4$. In the case of oxides, these modes are well separated from the rest of the modes. In sulfides, depending on the mass of the non-Lithium cations, these modes may or may not have contribution from lithium, the lighter the mass of the non-Lithium cations the better well separated are these modes. Li contribution tends to fall in the middle energy range in Lisicon and Low energy range in Olivine which have very important consequence on the migration barriers and will be discussed in detail in the next section. The contribution to the total DOS from the structural anions (O$^2-$ or S$^2-$) tend to dominated the low-energy part of the phonon DOS (Please refer to all the computed DOS in appendix E). Substituting oxygen in Li$_3$PO$_4$ (Pnma) by sulfur to form Li$_3$PS$_4$ (Pnma and Pnm21) led to a downshifting (softening) of lithium ion vibrations from 40-70 meV to 40-50 meV (Figure 3.4a and 3.4b). Aliovalent substitution of P$^{5+}$ by Ge$^{4+}$ induces strong broadening of features around 40-70 meV which primarily came from lithium ion vibrations in the phonon DOS (Figure 3.6a). No softening of the modes is observed upon aliovalent substitution. The broadening seems to increase with Ge$^{4+}$.
content in Li$_{3+x}$Ge$_x$V$_{1-x}$O$_4$, where $x = 0, 0.2, 0.4, 0.8$ and 1 (Li$_3$VO$_4$, LGVO20, LGVO40, LGVO80 and Li$_4$GeO$_4$) in Figure 3.6a. Again, the feature that is the most affected by this broadening is the one that originates mainly from Li-ion vibrations which is consistent with the increase of Li-ion concentration and mobility upon Ge$^{4+}$ substitution. Similar broadening of lithium phonon DOS was observed for Li$_{3.4}$Ge$_{0.4}$P$_{0.6}$O$_4$ (Pnma) and Li$_{3.25}$Ge$_{0.25}$P$_{0.75}$S$_4$ (Pnma) upon substituting P with Ge in Li$_3$PO$_4$ (Pnma) and Li$_3$PS$_4$ (Pmm2$_1$), respectively, as shown in Figure 3.4. We note that the broadening of ‘Lithium’ peak is more drastic in sulfides (Figure 3.4b and 3.4d) compared to oxides.
(Figure 3.4a and 3.4c) which seems to be consistent with the higher mobility of Li in thio-Lisicon. We attribute this broadening of lithium ion vibrations to the increase of disorder in Li sublattice by introducing defects into the LISICON structure such as increasing partial occupancy in the lithium sublattice. Another very informative observation is on the temperature dependence of phonon DOS shown in Figure 3.6b-3.6d. Comparing the phonon DOS of Li₃PO₄ and Li₃PS₄, we notice marked broadening of a peak around ~50 meV in phonon DOS of Li₃PS₄ upon increasing temperature from 100 K to 300 K while the phonon DOS of Li₃PO₄ remains essentially the identical. This broadening in Li₃PS₄ can be explained by noticing that the peak ~50 meV in the DOS comes almost entirely from the Li-sublattice vibration (Figure 3.4b). As the temperature increases, this peak broadens due greater lithium partial occupancy and large displacement amplitudes (anharmonicity) of lithium ions in Li₃PS₄ as expected from its low migration barrier (~0.5 eV), in agreement with the concept discussed in Figure 3.1. No broadening is observed upon increasing the temperature in Li₃PO₄ because the mobility of Li-ions and the partial lithium occupancy (or mobile lithium ion concentration) is very low (~2.05 x 10⁸/cm³ at 300 K using lithium vacancy formation energy of ~1.7 eV), and displacement amplitudes is expected to be small. Further support came from the observation that in Li₃PS₄, the low and high energy peaks in the DOS showed negligible changes with temperature since those peaks correspond to the non-mobile PS₄ tetrahedral units and the sulfur sublattice. Finally, Li₁₀SnP₂S₁₂ (isostructural to Li₁₀GeP₂S₁₂), with disordered lithium sublattice and liquid-like lithium ion conductivity at room temperature, 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 Figure 3.6d. These qualitative observations all support the idea that lattice dynamics have strong, clear and measurable influence/correlation with the ionic mobility in the lattice.

3.4 Correlation between phonon band center and migration barrier

3.4.1 Phonon band center

We will now give a more quantitative assessment between the lattice dynamics and mobility. To that end, first we recall from our initial idea give in the introduction where, using a rather intuitive conceptualization and the simple Einstein model, we arrive at the (semi-heuristic) conclusion that there must be some correlation between the migration barrier and the Einstein frequency. However, the very idea of Einstein frequency relies on a model assuming independent
Figure 3.7 a) Comparison between (neutron-weighted) computed phonon band center and the measured phonon band center. b) Correlation between the measured activation energy and the measured phonon band center. The data clearly separate into two groups, one for stoichiometric compounds, the other for non-stoichiometric compounds (with partial occupancy).

The question we were asking was how we can extend this notion from a model to a real material system. To address this question, we have drawn inspiration from the concept of Oxygen p-band center which have been used quite successfully to account for the activity and stability for perovskite in Oxygen evolution and reduction reactions. The Oxygen p-band center is defined as the centroid of the electronic DOS projected on the p orbitals of oxygens. In a similar vein, we define the phonon band center which is the centroid of the phonon DOS which can be computed using the following formula:

$$\omega_{av} = \frac{\int \omega \cdot DOS(\omega) d\omega}{DOS(\omega) d\omega} \quad (3.3)$$

Mathematically, this is the definition of an average quantity in the probabilistic sense where the probability distribution function is replaced by the phonon DOS. It can be view as the ‘average’ vibrational frequency of the lattice. From this definition, we can also define other related descriptor for example if we replace the total phonon DOS by the atom-projected DOS say Lithium, we can correspondingly define Li-phonon band center which can be thought of as the average vibrational frequency of Li sublattice.
Using the definition of phonon band center in Eq. (3.3) with the measured (total) phonon band center of several Lisicon compounds that we have synthesized (the details of synthesis conditions as well as the XRD spectra are given in appendix C) and compared them with the computed values. The results are shown in Figure 3.7a. The phonon band centers calculated from measured phonon DOS are systematically low than that calculated from the computed DOS. This is due to the issue we already mentioned regarding the red shift of the high energy modes in computed phonon DOS. However, the deviation is rather small and the trend is well preserved in the computed DOS. We don’t have the measured Li-projected phonon DOS due to the experimental complexity in deconvoluting the contribution of Li sublattice from the total DOS. However, we expect a better agreement between the measured and computed Li-band center since the Li-dominated part of the DOS tend to be restricted to the middle and low energy range which are less affected by the red-shift issue.

When we plot the measured activation energy of Li in Lisicon versus their phonon band center (Figure 3.7b), we found indeed a correlation, corroborating our hypothesis, but unexpectedly, we found that the data fall into two separate trends, one for the stoichiometric compounds without partial occupancy and the other for doped compounds with significant partial Li occupancy. The clear separation between the series of compounds with and without partial occupancy points to the free energy of defect formation as the underlying cause of the observed trend. Since we are more interested in the migration barrier of Li conductors, we will directly compute the enthalpy of migration using the climbing image nudge elastic band (NEB) method\textsuperscript{135}, which would allow us to systematically examine both stoichiometric LISICONs without partial occupancy and substituted LISICONs with partial occupancy Moreover, as the total phonon band center can be weighted considerably by the vibrations of non-mobile species such as structural (non-Li) cations and anions framework, we further sought correlations between the band center of lithium-projected phonon DOS and activation energy.

### 3.4.2 Calculation of migration in Lisicon and Olivine families

In NEB calculations, one has to specify in advance the jump sequences of diffusion paths whose migration barrier one wish to determine. In Olivine compound, it is obvious from the structure and the position of Li-ions what is the most likely diffusion path. However, in Lisicon, the lowest energy pathway is not obvious at all. In this study, we are not looking for the lowest
energy pathway in Lisicon. Instead, we would to focus on a particular jump sequence which is as close as possible to that in Olivine and examine how the migration barrier associated with this pathway change with the chemistry of the materials (i.e. changing cations and/or anions). Concretely, for Olivine, we choose the one-dimensional chain of edge-sharing octahedra described in section 3.2, create a vacancy by removing a (neutral) Lithium and compute the migration barrier associated with the jumps of the adjacent Li-ion into that vacancy (Figure 3.8a). The most ‘similar’ path in Lisicon is the one-dimensional chain of corner-sharing tetrahedra also described in detail in section 3.2 (Figure 3.8b). Similarly, we remove one Lithium from the chain and compute the migration barrier for the adjacent Li-ion to jump into the vacancy. The detail of the NEB calculation can be found in the appendix A.

The energy profile along the lowest energy pathway and the configuration of Li-ions along these paths are shown in Figure 3.8. In olivine, the jump sequences turn out to be oct \(\rightarrow\) tet \(\rightarrow\) oct where in the transition state, Li is in the tetrahedral environment which in some cases for example in
Figure 3.9 Correlation between the computed enthalpy of migration or migration barrier in Olivine and Lisicon with a) Total phonon band center and b) Lithium phonon band center. No clear correlation can be found for total band center but a very good correlation is found with Li band center.

LiMgVO₄ is a local minimum. In Lisicon, the geometry of the transition state is not very well defined. It is best described as an off-center triangle where Li-ion is located at the center. This configuration of transition state is always the maximum along the minimum energy pathway. As usual, the energy barrier $E_m$ is defined as the difference between the maximum along the pathway and the minimum which in our cases correspond to the initial and final configurations. The computed migration barrier (~0.3 eV) of LiMgPO₄ is in good agreement with previous computational results and NMR measurements for the site-to-site hopping (0.3 - 0.5 eV).¹³⁶

3.4.3 Results and discussions

Once we have the computed migration barrier (or enthalpy of migration if we neglect the PV term) and the phonon band center, we can now test our hypothesis which was state in section 3.1. First, we try to correlate the enthalpy of migration in Olivine and Lisicon (both LT and HT phases) with the total phonon band center (Figure 3.9a). However, unexpectedly, there is no correlation: the olivine compounds cluster separately while Lisicon compounds seem to cluster into oxides and sulfides. However, if instead of using total band center as the descript, we use the
Li phonon band center as descriptor, we found that there is remarkable correlation with the enthalpy of migration (Figure 3.9b). In retrospect, this correlation is somewhat expected since as we discussed earlier when we formulated the hypothesis regarding the connection between lattice dynamics and migration barriers, the frequency that should matter is that of the mobile specie which is Lithiums, that is why we find the correlation with the Li-band center which is a measure of the vibrational frequency of Li sublattice. Interestingly, the migration barriers in Olivine which are oxides comparable to that in thio-Lisicon and Lithium phonon band center can capture this subtle behavior which to the best of our knowledge can be captured by any other descriptor. We also note that, there seem to be a gap in the computed enthalpy of migration around 0.6 eV which gives the visual impression that the data in Figure 3.9b clusters into two regions. Unfortunately, this lack of data gap is beyond our control as all the compounds (existing and hypothetical) we include in our study don’t have the migration barrier that falls in that regions. Had we had more data to fill this gap, we believe that the correlation will appear much stronger. The correlation between enthalpy of migration and the Li phonon band center is one of the main result of this thesis which entirely supports with our hypothesis. In the next section, we will present another major result that is the correlation between the anion band center and the stability of Li-ion conductors.

3.5 Correlation between phonon band center and (electro)chemical stability of Li-ions conductors

As we mentioned in the introduction of this thesis, good ionic conductivity is only one of the properties the Li-ion conductors must have. In another very important criterion is stability either chemical or electrochemical. As we will see, good ionic conductivity and good stability tends to be mutually exclusive, good Li-ion conductors such as sulfides tend to have poor stability and vice-versa. In this section, we will present a new descriptor based on lattice dynamics that allows us to understand the stability trend among different Li-ion conductors. But first, we need to quantify the stability of ion conductor and this is achieved using a computational method which is described in detail in the next section.

3.5.1 Computation of stability window of solid state Li-ion conductors
Figure 3.10 Grand-potential phase diagram of Li$_3$PO$_4$ at different chemical potential of Lithium. At 0V versus Li, Li$_3$PO$_4$ is not stable and decomposes into Li$_3$P and Li$_2$O. Between ~0.7V and 4.2V versus Li, Li$_3$PO$_4$ since it is on the convex hull. This potential window is the stability window of Li$_3$PO$_4$.

In other to quantify the stability of a Li-ion conductors, we would like to calculate the
potential (vs Lithium metal) at which it become thermodynamically favorable to extract Li from the electrolytes (oxidation potential) as well as the potential at which Li is inserted into the electrolytes (reduction potential). The difference between oxidation and reduction potential is called the stability window of the electrolyte. Ideal solid Li electrolytes with will reduction potential as close as possible to zero so that it is stable against Li metal (negative) electrode and the oxidation potential as high as possible so the it is stable against high-voltage cathode.

To determine the oxidation and reduction potential, we adopt the method developed by other researchers\textsuperscript{28,137} which generalizes the traditional phase diagram to include the influence of Lithium chemical potential. Conceptually, we imagine that the electrolyte is in contact with a Li reservoir characterized by Li chemical potential $\mu_{Li}$ (think of the parallel with the thermal reservoir characterize by the temperature $T$). In this setting the relevant thermodynamics potential is the grand potential which is the Legendre’s transform of Gibbs free energy $G$ with respect to chemical potential of Lithium:

$$\Phi[c, \mu_{Li}] = G[c] - n_{Li}[c]\mu_{Li} = E[c] - TS + PV - n_{Li}[c]\mu_{Li}$$  \hfill (3.4)

Where $c$ is a composition and $n_{Li}$ is the fraction of Li in that composition, $E[c]$ is the internal energy. In practice, $E[c]$ is the energy obtained from DFT calculations and as DFT is a 0K method, the temperature is set to 0K. Moreover, we also neglect the PV term (which is small at ambient condition) so that at the end, the grand potential becomes:

$$\Phi[c, \mu_{Li}] = E[c] - n_{Li}[c]\mu_{Li}$$  \hfill (3.5)

Once the grand potential is defined, we can calculate this quantity for all compounds in a chemical system and construct the phase diagram using this quantity instead of the Gibbs free energy as in the conventional phase diagram. By doing so, the effect of chemical potential is readily taken into account by the definition of the grand potential itself. In this work, the compounds within a given chemical family are taken from the Materials Project database. An example of grand potential phase diagram of Li$_3$PO$_4$ constructed using this approach is given in Figure 3.10 at different voltage vs Li which is nothing but the chemical potential of Li. At 0V vs Li, Li$_3$PO$_4$ is not stable (as can be seen from the fact that it is above the convex hull) and decomposes into Li-rich compounds Li$_3$P and Li$_2$O. When we increase the potential to ~0.7V vs Li, Li$_3$PO$_4$ falls on the convex hull and thus becomes stable. This potential is called the reduction which is the potential below which the electrolytes is reduced by Li insertion and decompose into more Li-rich compounds. Above 0.7V, Li$_3$PO$_4$ remains stable until ~4.2V vs Li. Above this potential which is
Figure 3.11 Computed oxidation and reduction potential of all Lisicon and Olivines included in this study. The vertical bars correspond to the stability window of each electrolytes.

called oxidation potential, the electrolyte is oxidized by Li removal and decomposes into Li-deficient compounds. In case of Li$_3$PO$_4$, the electrolyte decomposes into elemental phosphorus accompanied by $O_2$ evolution. This calculation tells us that from the perspective of stability, Li$_3$PO$_4$ is a rather good electrolyte with relatively large stability window ~3.5V. Although it is not thermodynamically stable against Li, the relatively small reduction potential suggests that it might be kinetically stable in contact with Li.

The computed oxidation and reduction potentials of all Lisicon and Olivine compounds in this study are shown in Figure 3.11. These vertical bars correspond to the stability window of each electrolytes. As mentioned, sulfides tend to have smaller stability window than oxides. Interestingly, none of these electrolytes is thermodynamically stable against Li metal. Moreover, there is significant variation in the oxidation and reduction potentials among these compounds. As we will see shortly in the next section, these variations can be explained (partially) by the phonon band center that we introduced in section 3.4.
Olivine Li-ion conductors and the (phonon) anion band center.\(^{159}\)

### 3.5.2 Results and discussions

We found that the oxidation potential has a very strong correlation (goodness of fits \(R^2 = 0.97\)) with the anion phonon band center as shown in Figure 3.12a. We’ve also try to correlate the reduction potential with anion band center. However, no correlation was found (Figure 3.12b) and this absence of correlation remains an open question. Lowering the anion phonon band center was found to greatly reduce the stability of these LISICONs against electrochemical oxidation. 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. We would like also to point out an interesting observation regarding the Olivine compounds. Generally speaking, compounds having high Li conductivity tend to have low stability (Figure 3.9b and 3.12a), but Olivine family was found to be an exception to this trend, which was rationalized in terms of the exceptionally low Li-band center but high anion band center in these compounds (Figure 3.13). For example, new compositions such as LiMgAsO\(_4\) and LiInGeO\(_4\) could potentially have high ion conductivity (Figure 3.9b) and stability (Figure 3.13). Unfortunately, the presence of anti-site defects in Olivines\(^{136,141}\) has limited experimental demonstration of Olivine compounds with high ion conductivity to date although several strategies can be explored to solve this problem. Further studies are needed to increase the long-range ion conductivity of these Olivines by reducing anti-site defects using smaller particle sizes\(^{142}\) and/or having Li-excess in the lattice\(^{143}\), which would
Figure 3.13 Correlation between computed anion band centers and Li-band centers of Olivine compounds compared to LISICON compounds.\textsuperscript{159}

potentially lead to the development of lithium superionic conductors with high stability against electrochemical oxidation.

While oxidative stability can be understood in term of electronic structures of the electrolytes which correlate with the thermodynamics driving force to oxidize the materials, the correlation between the oxidation potential and the anion band center 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 (kinetics property), which promotes the kinetics of reactions. This kinetics property, by the Evans-Polanyi principle\textsuperscript{144}, correlates with oxidative
Figure 3.14 Correlations between the oxidation potential and a) computed Li-band center b) computed total-band center. Absence of correlation between reduction potential and c) Anion, d) Lithium and e) Total band center. f) The downshifting of anion band center is broadly accompanied by the downshifting of Li-band center. The numbers in the plots refer to: 1. Li$_3$PO$_4$ 2. Li$_3$VO$_4$ 3. Li$_3$AsO$_4$ 4. Li$_2$CdGeO$_4$ 5. Li$_2$CdGeS$_4$ 6. Li$_2$CdGeSe$_4$ 7. Li$_2$CdSiS$_4$ 8. Li$_2$CdSnS$_4$ 9. Li$_3$PS$_4$ 10. Li$_3$AsS$_4$ 11. Li$_3$GeS$_4$ 12. Li$_2$MgGeO$_4$ 13. Li$_2$CdSiO$_4$ and 14. Li$_3$Ge$_{0.25}$P$_{0.75}$S$_4$.

stability (thermodynamics property) as measured by the oxidation potential. We recognize that
Figure 3.15 Absence of correlation between a) oxidation potential and anion p-band center b) Anion p-band center and anion phonon band center.  

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. The computed oxidation potential of Li$_3$PO$_4$ (Pnm2$_1$) and Li$_3$PS$_4$ (Pnma) are in agreement with previous computation. The computed oxidation potential of Li$_{3.25}$Ge$_{0.25}$P$_{0.75}$S$_4$ is 0.21 V vs. lithium, which is close to the measured oxidation potential of chemically similar Li$_{10}$GeP$_2$S$_{12}$. We have also attempted to correlate the oxidation potential and reduction potential with other phonon band centers. We found that oxidation potentials also correlate with the Lithium and total phonon band center albeit with lower goodness of fit compared to anion band center ($R^2 = 0.91$ for Li and $R^2 = 0.93$ for total band center) (Figure 3.14). There was no correlation between the reduction potential and the phonon band centers (Figure 3.14), whose physical origin requires further studies. We also seek correlation between oxidation potential and oxygen/Sulphur p-band center which have been used to study the stability of perovskites under oxygen evolution reaction condition. However, as can be seen from Figure 3.15a and 3.15b, there is no clear correlation between p-band center and the oxidation potential or the anion band center although we can note that the oxidation potential is largely determined by the anion chemistry (oxides vs sulfides) as reported previously in the literature and that oxides tend to have lower anion p-band center than sulfides as expected. It should be noted that the absence of correlation might also be due, at least partly, to the uncertainty in the computed p-band center arising from the underestimation of DFT band gap in these.
insulating compounds. Therefore, the anion band center is proposed as one descriptor for electrochemical oxidation stability of lithium ion conductors. 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 Figure 3.1 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.
Lattice Dynamics and Meyer-Neldel Rule in Li₃PO₄ - Li₃VO₄ - Li₄GeO₄ System

In previous chapter, we focused mainly on the influence of the lattice dynamics through phonon band centers on the migration barrier and stability of Li-ion conductors. The vast majority of current research to increase lithium ion conductivity, is directed towards lowering energetic barrier (Eₐ) for lithium ion migration in the structure. However, in addition to the activation energy, there is also another knob to tune the ionic conductivity which is the pre-exponential factor σₒ as can be seen from the Arrhenius equation. This fact seems to be overlooked by the community whose focus has been mainly on varying the activation energy. The reason behind this lack of interest seems to be related to the fact that the pre-exponential factors is much less well understood as it depends on many different parameters in particular the entropy of migration Sₘ which aren’t well characterized experimentally nor computationally. Moreover, it is also known that the pre-exponential factor and the activation energy are not independent from one another. For example, West et al. have shown that lowering the activation energy from 1.0 to 0.6 eV is accompanied with a decreased pre-exponential factor, σₒ, of LISICON Li₂+2xZn₁-xGeO₄ solid solutions by ~6 orders of magnitude. The correlation between pre-exponential factor and the activation energy is not limited to ionic conductivity but seems to be applicable to any thermally activated process such as reaction kinetics where it called iso-kinetic rule or compensation law in the chemical kinetics community. The correlation between σₒ and Eₐ can be rationalized by invoking a linear relation Sₘ = Eₘ/Tₒ where Tₒ is related to the temperature of lithium sublattice disordering or Sₘ/k_B = Eₘ/Δₒ to yield Δₒ which is the energy scale of the excitation in the system according to the Multi-Excitation Entropy theory and represents the inverse of the slope in a Meyer-Neldel plot. We will also shed new light on this correlation by showing for the first time that the intercept in the Meyer-Neldel plot can be related to the Gibbs free energy of defect formation. We will first narrow our discussion to a model system which is the solid solution of
4.1 \(\text{Li}_3\text{PO}_4 - \text{Li}_3\text{VO}_4 - \text{Li}_4\text{GeO}_4\) solid solutions as model system

4.1.1 Material synthesis and characterizations

In order to study the correlation between pre-exponential factors and activation energy, we choose to focus on the \(\text{Li}_3\text{PO}_4 - \text{Li}_3\text{VO}_4 - \text{Li}_4\text{GeO}_4\) solid solution as our model system. The synthesis, characterization and EIS measurements were done by John C. Bachman. Starting with \(\text{Li}_3\text{PO}_4\) we progressively substitute \(\text{P}^{5+}\) with isovalent cation \(\text{V}^{5+}\) in order to study the effect of cation. We also did aliovalent substitution with \(\text{Ge}^{4+}\) to study the effect of changing the density of mobile charge carrier. The schematic of this substitution strategy is shown in Figure 4.1a. The detail condition for the material synthesis and XRD characterization are given in appendix C. From the XRD patterns, we can conclude that the samples are phase-pure and from the table C.1 also given in the appendix C, the stoichiometries of the sample are very close to the expected ratio from the target compositions indicating that there is no Li-deficiency in the samples during the
Figure 4.2 Scanning electron microscope images of fractured pellets of Li$_3$PO$_4$, Li$_3$VO$_4$, Li$_4$C
Li$_3.4$Ge$_0.4$P$_0.6$O$_4$, Li$_3.4$Ge$_0.4$V$_0.6$O$_4$, and Li$_3$V$_0.4$P$_0.6$O$_4$. Preparation. The volume of the unit cell obtained from fitting with the XRD patterns increase linearly with the average ionic radius of the non-Lithium cations as expected (Figure 4.1b). The average radii were computed by adding the Shannon radius of each non-lithium cation weighted by their corresponding fraction in each sample. The unit cell volume for compounds with $Pmn2_1$ symmetry were multiplied by two as the number of formula units is two in $Pmn2_1$ and four in $Pnma$ and $Cmcm$. 
Scanning electron microscope images of fractured pellets of Li$_3$PO$_4$, Li$_3$VO$_4$, Li$_4$GeO$_4$, Li$_{3.4}$Ge$_{0.4}$P$_{0.6}$O$_4$, Li$_{3.4}$Ge$_{0.4}$V$_{0.6}$O$_4$, and Li$_3$V$_{0.4}$P$_{0.6}$O$_4$ were taken and shown in Figure 4.2. Li$_3$PO$_4$ and Li$_{3.4}$Ge$_{0.4}$P$_{0.6}$O$_4$ showed little porosity with grain sizes of 10-20 µm, which are in agreement with the porosity measurements of 7% and 9%, respectively. Li$_3$VO$_4$, Li$_4$GeO$_4$, Li$_{3.4}$Ge$_{0.4}$V$_{0.6}$O$_4$, and Li$_3$V$_{0.4}$P$_{0.6}$O$_4$ images showed some secondary morphology with nano-porosity, which agrees with the higher porosities of 13%, 24%, 17%, and 13% found, respectively. The porosity of sintered pellets was determined by measurement with a micrometer, which was consistent with scanning electron microscope (SEM) secondary electron images of fractured cross-sections of pellets on a Zeiss Merlin SEM. Samples with germanium content showed carbon content from energy-dispersive x-ray spectroscopy, most likely due to surface Li$_2$CO$_3$ from exposure to air before imaging. No Li$_2$CO$_3$ was found within samples from x-ray diffraction.

4.1.2 Lithium Ion conductivity of Li$_3$P$_{1-x}$V$_x$O$_4$, Li$_{3-x}$V$_{1-x}$Ge$_x$O$_4$ and Li$_{3-x}$P$_{1-x}$Ge$_x$O$_4$ (x = 0, 0.2, 0.4, 0.6, 0.8 and 1)

The procedure for samples preparation for Electrical Impedance Spectroscopy (EIS) measurements as well as the conditions and the equivalent circuits used to extract the bulk and grain boundary conductivity are given in detail in appendix D. The conductivity data extracted from those measurements are shown in Figure 4.3 and 4.4. For LISICONs without partial lithium occupancy (Li$_3$P$_{1-x}$V$_x$O$_4$ (x = 0, 0.2, 0.4, 0.6, 0.8 and 1) and Li$_4$GeO$_4$), the EIS measurements yield values of ~2x10$^{-10}$ S/cm for Li$_3$PO$_4$ and ~2x10$^{-9}$ S/cm for Li$_4$GeO$_4$ at 100 °C, which are consistent with previous reports. In addition, these conductors were found to have high activation energy of ~1.1 eV (Figure 4.3), in agreement with previous studies$^{57}$, which can be attributed to both enthalpy migration and enthalpy of defect formation. Isovalent substitution of P$^{5+}$ for V$^{5+}$ for in the crystal structure (space group $Pnma$) did not lead to any noticeable changes in the ion conductivity nor activation energy as expected. In contrast, aliovalent substitution of P$^{5+}$ or V$^{5+}$ for Ge$^{4+}$ in Li$_3$PO$_4$ and Li$_3$VO$_4$ that creates partial lithium occupancy showed much higher conductivity and lower activation energy, as shown in Figure 4.3. Aliovalent substitution of P$^{5+}$ or V$^{5+}$ by Ge$^{4+}$ by 20% led to marked increase in lithium ion conductivity by 4-5 orders of magnitude relative to Li$_3$PO$_4$ and Li$_3$VO$_4$ in Figure 4.3b. This increase is accompanied with large reduction in the activation energy of ~0.5 eV in Figure 4.3c, which can be attributed to the reduction of formation
Figure 4.3 a) Arrhenius plot of Li$_{3-\delta}$V$_{1-x}$O$_4$, Li$_{3+\delta}$V$_{1-x}$Ge$_{\delta}$O$_4$ and Li$_{3+\delta}$P$_{1-x}$Ge$_{\delta}$O$_4$ (x = 0, 0.2, 0.6, 0.8 and 1). For compounds with partial Li occupancy, the conductivity reported here are conductivity. b) Conductivity at 30 °C and c) Activation energy of Li$_{3+\delta}$P$_{1-x}$Ge$_{\delta}$O$_4$, Li$_{3+\delta}$V$_{1-x}$Ge$_{\delta}$O$_4$, and Li$_{3+\delta}$P$_{1-x}$V$_{1-x}$O$_4$ (x = 0, 0.2, 0.4, 0.6, 0.8 and 1). The conductivity of all compound with partial Li occupancy were extrapolated from high-temperature measurements.\textsuperscript{195}

enthalpy of mobile charge carrier in the activation energy for lithium ion conduction with partial lithium occupancy. Further increasing the amount of Ge$^{4+}$ substitution in Li$_3$PO$_4$ and Li$_3$VO$_4$ did not result in any significant changes in the lithium ion conductivity (Figure 4.3b) while the activation energy was found to increase gradually with greater Ge substitution in Figure 4.3c, which can be attributed to increasing migration barrier with increasing Ge$^{4+}$ ion in the crystal structure. This trend cannot be explained by the variation in the volume of the unit cell as can be
seen from Figure 4.4a, the unit cell volume of the \( \text{Li}_{3+x}\text{V}_{1-x}\text{Ge}_x\text{O}_4 \) series barely changes while that of the \( \text{Li}_{3+x}\text{P}_{1-x}\text{Ge}_x\text{O}_4 \) series increases with Ge content. We explain this trend in terms of inductive effect\(^{151}\) by which Ge\(^{4+}\) which is less positively charge than P\(^{5+}\) or V\(^{5+}\) pulls less electron density from oxygen resulting in higher effective charge on oxygen which in turns leads to stronger electrostatic interaction with Li\(^+\) and higher activation energy. This trend is also consistent with variation in activation energy found in the lithium superionic conductor \( \text{Li}_{10}\text{Ge}_{1-x}\text{Sn}_x\text{P}_2\text{S}_12 \) series.\(^{152}\) While the variation of the unit cell volume can be excluded as one possible explanation for the observed trend of activation energy as a function of Ge content, we cannot entirely exclude subtler structural changes such as polyhedral volumes or the size of the ‘diffusion pathway’ which require a more detailed analysis of atomic positions in the unit cell.

4.1.3 Classical Molecular dynamics simulations of \( \text{Li}_{3+x}\text{V}_{1-x}\text{Ge}_x\text{O}_4 \) (\( x = 0.2, 0.4, 0.6, 0.8 \) and 1)

In order to further understand the effect of aliovalent substitution on the activation energy of Lisicon, we have performed classical MD simulations (the computational details are given in appendix A) on the series \( \text{Li}_{3+x}\text{V}_{1-x}\text{Ge}_x\text{O}_4 \) (\( x = 0.2, 0.4, 0.6, 0.8 \) and 1) at different temperatures. From the MD trajectories, we can plot the mean square displacement as a function of time, the slope of which is related to the self-diffusion coefficient (diffusivity). The results of these
Figure 4.5 a) The computed (self) diffusion coefficient of Li$_{3+x}$Ge$_x$V$_{1-x}$O$_4$ (x = 0.2, 0.4, 0.6, 0.8 and 1). b) Comparison between the computed and measured activation energy. Simulations are shown in Figure 4.5. With increasing Ge substitution in Li$_{3+x}$Ge$_x$V$_{1-x}$O$_4$, the computed activation energy for lithium diffusion was increased, which suggest that the observed increase in the activation energy of lithium ion conductivity result from increasing lithium migration/diffusion enthalpic barrier. It should be noted that computed activation energy for lithium diffusion was slightly smaller than measured for compositions with partial occupancy while the computed activation energy of Li$_4$GeO$_4$ was higher than the experimental value. Many factors including differences in the stoichiometry, unit cell sizes, and the absence of grain boundary and porosity in the MD simulation can contribute to this discrepancy.

We have also computed Li ions density (probability distribution) from the MD trajectories to provide important information on the diffusion mechanism and pathway in a given material. The Li ion probability distribution in Li$_{3.6}$Ge$_{0.6}$V$_{0.4}$O$_4$ at 1000 K is plotted in Figure 4.6a-4.6c at three different values of probability (P). The regions with high value of probability (Figure 4.6a) correspond to the equilibrium positions of lithium in the structure. As we systematically lower the value of probability density, these regions expand and eventually form a percolating network. Interestingly, we found that at $P \approx 8 \times 10^{-5}$ (Figure 4.6b), there are two percolating sub-networks parallel two (001) planes indicating that most facile diffusion pathways are actually ‘quasi two dimensional’ and the jump sequences along c-axis that connect these two regions are associated
Figure 4.6 Isosurface of Li$^+$ probability distribution function in Li$_{3.6}$Ge$_{0.6}$V$_{0.4}$O$_4$ at 1000 K calculated from the MD trajectories at different values of probability $P$. Regions with high value of $P$ corresponds to the equilibrium position equilibrium positions of lithium ions in the crystal. By reducing the value of $P$, we can visualize the regions less frequented by lithium-ions. This percolated region can be viewed as the diffusion pathway for lithium in the structure.$^{195}$

with higher activation barrier. At even lower value of probability density (Figure 6c), these two sub-networks percolate and form a three-dimensional network over the entire lattice.

In order to have a more detailed understanding of the dynamics of lithium sublattice, we have also computed the Van Hove correlation function$^{117}$ of Li$_{3.6}$Ge$_{0.6}$V$_{0.4}$O$_4$ and Li$_4$GeO$_4$ at 1000 K, which are shown in Figure 4.7. The Van Hove correlation function can be separated into two parts: the self-part $G_s(r, t)$ which is related to the probability to find Li ions at the distance $r$ at time $t$ from their original position and the distinct-part $G_d(r, t)$ which is related to the probability to find the ions $j$ at distance $r$ at time $t$ from the initial position of ions $i$ ($i \neq j$) and which is reduced to the static pair correlation function at $t = 0$. The self-part of Van Hove correlation function of Li$_{3.6}$Ge$_{0.6}$V$_{0.4}$O$_4$ and Li$_4$GeO$_4$ are shown in Figure 4.7a and 4.7b. For Li$_{3.6}$Ge$_{0.6}$V$_{0.4}$O$_4$, there is an intense feature close to the origin which corresponds to the local oscillations of Li-ions around their equilibrium position. This feature dies out relatively fast accompanied by the emergence of new features at $\sim 3$ Å away which correspond to jumps of Li-ions to neighboring positions. In contrast, in Li$_4$GeO$_4$, the intense feature close to the origin persists over much longer period of
Figure 4.7 Self-part of the Van Hove correlation function of a) Li$_{3.6}$Ge$_{0.6}$V$_{0.4}$O$_4$ and b) Li$_4$GeO$_4$ at 1000 K. Distinct-part of the Van Hove correlation function of c) Li$_{3.6}$Ge$_{0.6}$V$_{0.4}$O$_4$ and d) Li$_4$GeO$_4$ at 1000 K. In Li$_{3.6}$Ge$_{0.6}$V$_{0.4}$O$_4$, the intense feature close to the origin decay quickly as function of time with an early emergence of new features at ~2-3 Å from the origin corresponding to the jump of lithium ions to the neighboring positions. In contrast, in Li$_4$GeO$_4$, the feature near the origin decays much more slowly with the appearance of new feature around 2 Å at much later time, reflecting the low ionic conductivity in this compound compared to Li$_{3.6}$Ge$_{0.6}$V$_{0.4}$O$_4$. The intense peaks close to $r = 0$ are indicative of the correlated nature of the Li ions motion in these materials and correspond to the jumps of a Li ion to a neighboring site which were previously
Figure 4.8 Log of pre-exponential factor $\sigma_0$ from $\sigma T = \sigma_0 \exp(-E_a/kT)$ versus activation energy, $E_a$. Error bars show standard deviation of 2-3 samples for each composition. The compounds with and without partial occupancy falls on two separate lines with similar slopes. The intercept is related to the Gibbs free energy of defect formation.195

occupied by another ion. The onset of these peaks occurs sooner in Li$_{3.6}$Ge$_{0.6}$V$_{0.4}$O$_4$ compared to Li$_4$GeO$_4$, again in agreement with the fact that Li ions are more mobile in non-stoichiometric compositions. These findings are in close agreement with previous studies on Li$_3$PO$_4$-Li$_4$SiO$_4$-Li$_5$AlO$_5$ system153,154 and on doped Na conductor Na$_3$PS$_4$.155

4.2 Meyer-Neldel Rule in Li-ion conductors

4.2.1 Observation of Meyer-Neldel behavior in Li$_3$PO$_4$-Li$_3$VO$_4$-Li$_4$GeO$_4$

As mention in the introduction, the pre-exponential factor and the activation energy were found to be inter-dependent, a correlation known as the Meyer-Neldel rule.146,150,156 We have indeed found that this correlation also exists in our model system Li$_3$PO$_4$ - Li$_3$VO$_4$ - Li$_4$GeO$_4$
(Figure 4.8) but surprisingly, we found that the fall onto two separate lines with similar slopes but different intercepts. One set of data corresponds to compound without partial occupancy and the other set with partial occupancy. This observation hints at the defect formation energy as the origin behind the difference in the intercept on the y-axis. We will show rigorously in the next section that this is indeed the case and provides a simple way to estimate this value from the Meyer-Neldel plot.

4.2.2 Physical origin of the Meyer-Neldel Rule and the physical interpretation of the intercept in the Meyer-Neldel plot

The correlation between the pre-exponential factor and activation energy as well as the physical interpretation of the intercept in the Meyer-Neldel plot can be explained nicely by postulating a linear relation $S_m = E_m/T_0$ where $T_0$ is related to the temperature scale or equivalently $S_m/k_B = E_m/\Delta_0$ where $\Delta_0$ can now be viewed as an energy scale. We will provide the physical origin of this relationship later but now will show that with this relationship and the microscopic model of diffusion, we can rationalize all the data that we have at our disposition.

First, we know that the temperature-dependent ionic conductivity in crystalline materials follows Arrhenius law:

$$\sigma T = \sigma_0 \exp\left(\frac{-E_a}{k_B T}\right)$$

(4.1)

$\sigma_0$ and $E_a$ are respectively the pre-exponential factor and activation energy given by:30

$$\sigma_0 = \frac{zfq^2ad^2c_0v_0 \exp\left(\frac{S_m + S_f}{2k_B}\right)}{H_Rk_B}$$

and

$$E_a = H_m + \frac{H_f}{2}$$

Where $H_m$ is the enthalpy of migration, $H_f$ is the enthalpy of defect formation, $S_m$ is the entropy of migration and $S_f$ is the entropy of defect formation. $z$ is the number of neighboring positions with equal free energy, $f$ is the jump correlation factor, $q$ is the elementary charge, $\alpha$ is the inverse of two times the number of dimension, $d$ is the distance between the locations with equal free energy, $c_0$ is maximum concentration of charge carriers, $v_0$ is the jump-attempt frequency, $H_R$ is the Haven ratio. These parameters are not strongly material-dependent and in this work, we assume that $z = 4, f = 1, H_R = 1, \alpha = 1/6, d = 3.5 \text{ Å}$ and $v_o = 1 \text{ THz}$. 

74
Let define $\sigma_{oo}$ as $\sigma_{oo} = \frac{zq^2\alpha d^2\varepsilon_0}{H_R k_B}$ and take the natural logarithm on both sides of $\sigma_o$ we get:

$$\ln(\sigma_o) = \ln(\sigma_{oo}) + \frac{S_m}{k_B} + \frac{S_f}{2k_B}$$

(4.2)

We now make a crucial assumption that will be justified later, namely the linear relationship between the entropy of migration $S_m$ and the migration barrier $E_m$:

$$\frac{S_m}{k_B} = \frac{E_m}{\Delta_o} \approx \frac{H_m}{\Delta_o}$$

(4.3)

Replacing this expression into $\ln(\sigma_o)$ we get:

$$\ln(\sigma_o) = \ln(\sigma_{oo}) + \frac{H_m}{\Delta_o} + \frac{S_f}{2k_B}$$

(4.4)

We also have that:

$$H_m = E_a - \frac{H_f}{2}$$

(4.5)

Replacing this expression back into $\ln(\sigma_o)$ we get:

$$\ln(\sigma_o) = \ln(\sigma_{oo}) + \frac{E_a}{\Delta_o} - \frac{H_f}{2\Delta_o} + \frac{S_f}{2k_B} = \ln(\sigma_{oo}) + \frac{E_a}{\Delta_o} - \frac{H_f - T_o S_f}{2\Delta_o}$$

(4.6)

Where $T_o \equiv \Delta_o/k_B$. Since $H_f - T_o S_f = G_f(T_o)$, we arrive finally at our result:

$$\ln(\sigma_o) = \ln(\sigma_{oo}) - \frac{G_f(T_o)}{2\Delta_o} + \frac{E_a}{\Delta_o}$$

(4.7)

Which is the mathematical expression of the Meyer-Neldel rule. From the Eq. (4.7), it is now clear that the slope of the Meyer-Neldel plot is related to the energy scale $\Delta_o$ and the intercept the Gibbs free energy of defect formation (at $T_o$).

We now come back to the crucial assumption we made earlier to in the derivation of Eq. (4.7) namely the linearly relationship between $S_m$ and $E_m$ and will be the occasion to clarify the physical of these relationships. Regarding the relation, $S_m = E_m/\Delta_o$, it has been proposed that we can interpret $T_o$ as a ‘disordering’ temperature as it can be shown very easily that this relation implies that the free energy of migration $G_m$ is zero at $T_o$, i.e., $G_m(T_o) = 0$. This is reminiscent of a phase transition. The issue with this interpretation is that no clear physical ‘signature’ of $T_o$ has been reported so far. For instance, temperature-dependent ionic conductivity data shows no
discontinuity across $T_o$. One should note that $G_m$ is not a thermodynamic function or potential, it is the difference between the Gibbs free energy of the equilibrium configuration and the transition state. Therefore, the absence of a discontinuity that signals a phase transition is not very surprising although this will render experimental confirmation of $T_o$ much more challenging.

In this work, we adopt the alternative interpretation of the linear relationship between $S_m$ and $E_m$ from the energy perspective namely $S_m$ is related to $E_m$ via $S_m/k_B = E_m/\Delta_o$ where $\Delta_o$ is an energy scale. The precise nature of this energy scale is given by the multi-excitation entropy (MEE)\textsuperscript{149,150} that we will sketch the outline below.

Imagine that in the phase-space, the system (in our case, a system is the Li-ion conductor, we use the word system as this discussion also applies to other systems for example chemical reactions) is in a local minimum. Due to thermal excitation, the system can over the energetic barrier and be in another local minimum (we exclude quantum tunneling). Let’s denote this energy barrier $E_m$. To overcome this barrier, the system need to gain at least this amount of energy from the thermal excitation. In solids, the thermal excitation are phonons. Assume that system needs to absorb $n$ excitations to get the energy $E_m$ required to overcome the barrier. Let $\hbar \omega$ be the energy of each excitation. Hence:

$$E_m = n\hbar \omega$$ \hspace{1cm} (4.8)

However, the number of excitations (phonons) in the system is much larger than $n$ in general. Let’s call the total number of excitation in the system $N$. The entropy arises due to the multiple ways that we can choose $n$ excitations out of $N$ total excitations in the system. Using the well-known Boltzmann formula for entropy, we can write:

$$S_m = k_B \ln \left[ \frac{N!}{n!(N-n)!} \right] \approx k_B \ln(N) = \frac{k_B E_m \ln(N)}{\hbar \omega}$$ \hspace{1cm} (4.9)

We use the Sterling approximation in the 2\textsuperscript{nd} equality and replace $n$ from the Eq. (4.8) to get to the 3\textsuperscript{rd} equality. By comparing this equality with linear relation $S_m/k_B = E_m/\Delta_o$, we can identify $\Delta_o$ as:

$$\Delta_o = \frac{\hbar \omega}{\ln(N)}$$ \hspace{1cm} (4.10)

This equality indicates that $\Delta_o$ is related to $\hbar \omega$ which is the energy of phonon excitation in the systems. Obviously, due to very drastic approximation, we used to arrive at this result, it is accurate enough to provide quantitative prediction or verification. In particular, in the above
Figure 4.9 Plot of pre-exponential factor versus activation of a) Li$_{4-2x}$Zn$_x$GeO$_4$ b) Li$_{3+x}$Ge$_x$P$_{1-x}$S$_4$ c) Li$_6$P$_x$S$_5$Cl$_{1-x}$Br$_x$ and d) Li$_3$La$_3$Nb$_{2-x}$Y$_x$O$_{12}$. The (inverse of) the slope is related to the energy scale of the excitation (phonon) in the materials $\Delta_0$ and the intercept is related to Gibbs free energy of defect formation.\textsuperscript{195}

derivation we made implicit assumption that all phonons have the same energy, the phonon DOS is just a constant and that the ‘phonon-ion’ coupling constant or cross section is equal to one. The two former approximation can easily be made more rigorous. However, the computation of ‘phonon-ion’ coupling matrix is extremely hard and to the best of our knowledge has not been define rigorously let alone computed with sufficient accuracy. Nevertheless, this approach provides us enough information to be tested against experimental values of $\Delta_0$ which can be estimated from the slope the Meyer-Neldel plot as we’ve shown previously. In the following
Figure 4.10 Correlation of the phonon energy scale $\Delta_\omega$ as estimated from the inverse of the slope of the Meyer-Neldel plot as functions of a) Li-band center, b) Anion-band center, c) Total-band center and d) Computed Debye temperature. $\Delta_\omega$ seems to decrease with increasing phonon band centers.\textsuperscript{195}

In this section, we will provide the values of $\Delta_\omega$ of several Li-ions conductors and discuss the validity and consistency of our analysis as well as the implication of Eq. (4.7) by extending our discussion to include other Li-ion conductors whose ionic conductivity has been reported in the literature.

### 4.2.3 Extension to other Li-ion conductors

The Meyer-Neldel plots of 4 different Li-ion conductors $\text{Li}_{4.2x}\text{Zn}_x\text{GeO}_4$,\textsuperscript{58} $\text{Li}_{3+x}\text{Ge}_x\text{P}_{1-x}\text{S}_4$,\textsuperscript{42} $\text{Li}_6\text{PS}_3\text{Cl}_{1-x}\text{Br}_x$,\textsuperscript{83} $\text{Li}_5\text{La}_3\text{Nb}_{2-x}\text{Y}_x\text{O}_{12}$\textsuperscript{157} as well as the corresponding values of $\Delta_\omega$ are shown in Figure 4.9. The values of $\Delta_\omega$ for the series of compounds with and without partial Li occupancy...
Figure 4.11 Gibbs free energy of formation of mobile charge carrier estimated from the intercept of Meyer-Neldel plots using Eq. (4.7) in the main text for some common Li-ion conductors. The order of magnitude is reasonable (~1 eV) and expected, the defect formation energy is sulfides is smaller than oxides and decreases upon aliovalent substitution.\textsuperscript{195}

are 33.5 meV and 39.5 meV, respectively. These values are very similar, reflecting the closeness in ‘phonon energy’ in these two chemically similar series of compounds. Meyer-Neldel rule can also be found in other Li-ion conductors such as Lisicon Li\textsubscript{1.25}Zn\textsubscript{0.75}GeO\textsubscript{4} (Figure 4.9a), thio-Lisicon Li\textsubscript{3.75}Ge\textsubscript{x}P\textsubscript{1-x}S\textsubscript{4} (Figure 4.9b), Li\textsubscript{6}PS\textsubscript{3}Cl\textsubscript{1-x}Br\textsubscript{x} (Figure 4.9c) and garnet Li\textsubscript{3}La\textsubscript{1}Nb\textsubscript{2-x}Y\textsubscript{x}O\textsubscript{12} (Figure 4.9d). $\Delta_0$ in these materials were found to be ~15 - 60 meV which correspond well to the energy scale of phonon in solids which confirms the predictions of the MEE that we presented in previous section.

In other to further quantify this phonon energy scale, we use the (computed) Debye temperature\textsuperscript{158} as well as phonon band centers which were recently proposed as descriptor for enthalpy of migration in LISICON and Olivine compounds.\textsuperscript{159} As be seen from Figure 4.10, $\Delta_0$ seems to decrease with increasing phonon band center and Debye temperature. Obviously, more data are needed to confirm this trend whose physical origin is still an open question.

We have also estimated the Gibbs free energy of mobile carrier formation in some Li-ions conductors from the intercept with the y-axis using Eq. (4.7) and obtained reasonable values ~0.5
Figure 4.12 a) Plot of pre-exponential factor versus activation energy for several families of Li-ion conductors. Different families of Li-ion conductors exhibit different slopes and intercepts reflecting the different in their phonon energy and Gibbs free energy of defect formation. b) After rescaling the pre-exponential factor and activation energy using Eq. (4.7), all the points collapse on a single straight line with the slope of 1 as expected.  

-2 eV (Figure 4.11a), which is in agreement with previous work. For example, the formation energy of Frenkel defects in $\gamma$-Li$_3$PO$_4$ was found to be $\sim$ 1.7 eV from previous computational study. Moreover, as expected, the Gibbs free energy of defect formation decreases upon aliovalent substitution, as shown in Figure 4.11b for Lisicon and garnets. Finally, we have also compiled the values of pre-exponential factors and activation energy of several compounds from the literature and plot them in Figure 4.12a. The reference for the data of each series compound included here are Li$_{4-2x}$Zn$_x$GeO$_4$, Li$_{3+x}$V$_{1-x}$GeO$_4$, Li$_{3+x}$As$_{1-x}$Ti$_x$O$_4$, Nasicon-like LiX(PO$_4$)$_3$, Li$_{4-x}$Ge$_x$P$_y$S$_4$, Li$_{3+x}$Ge$_x$As$_1$-$_x$S$_4$, Li$_{4-x}$Sn$_{1-x}$As$_x$S$_4$, Li$_{10}$Ge$_1$-$_x$Sn$_x$P$_2$S$_{12}$, Li$_{10}$Ge$_1$-$_x$Sn$_x$S$_{12}$, Li$_3$X$_3$Te$_2$O$_{12}$, Li$_3$La$_3$Nb$_{2-x}$Y$_x$O$_{12}$, Li$_6$Al$_2$Ta$_2$O$_{12}$, Li$_6$Al$_2$Nb$_2$O$_{12}$, Li$_6$BaLa$_2$Nb$_2$Ta$_2$O$_{12}$, and Li$_6$PS$_5$Cl$_{1-x}$Br$_x$. Although within each family of compounds, the data follow Meyer-Nedel’s rule, their slopes and intercepts are different, reflecting the difference in the phonon energy scale and the Gibbs free energy of defect formation in these materials. However, based on Eq. (4.7), it is possible to rescale this data so that they collapse on the same straight line by normalizing $E_a$ by $\Delta_0$ and switch the second term containing $G_f$ to the left-hand side. The rescaled shown in Figure 9b, fall indeed on the same straight line with the expected slope of 1, confirming the validity of Meyer-Nedel’s rule and the consistency of our analysis.
Notice that in this analysis, $G_f$ and $\Delta_0$ were both extracted from Meyer-Neldel plot making the scaling in Figure 4.12b rather trivial. However, if one can get the values of $G_f$ or $\Delta_0$ from separate measurements or computations, this scaling analysis would provide much stronger evidence for the universality of Meyer-Neldel rule and its physical origin in terms of multi-excitation entropy. Understanding the physical origin behind this violation of Meyer-Neldel rule represents an exciting fundamental research opportunity that can also lead to new strategies to increase ionic conductivity by breaking this scaling relation.
Conclusions and Outlooks

In this thesis, 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 \(\alpha\)-AgI phonon DOS) or zone-center phonons as measured from infrared and Raman spectroscopy,\(^{167,168}\) 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. 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. 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 families beyond LISICON and Olivine. 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 leaning model...
to predict phonon-related properties such as vibrational free energy and entropy with high accuracy at a greatly reduced computational cost. 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. In the following sections, we will discuss in more detail some of the challenges and opportunities that to the author’s opinion are natural continuation of this thesis.
5.1 Influence of lattice dynamics in other ionic conductors

The argument we presented in chapter leading to the correlation between migration barrier and vibration frequencies (as measured by the phonon band centers) is not limited to Li-ion conductors. Indeed, there have been works suggesting that lattice dynamics also influence the ionic conductivity or mobility in other ionic conductors. For instance, as mentioned in chapter 3, Wakamura has suggested that the activation energy might correlates with ‘low-energy’ optical phonon. Moreover, lattice dynamics was also found to play important role in the Na\(^+\) conductors Na\(_3\)PS\(_4\)\(_x\)Se\(_x\)\(^{156}\) as well as O\(^2\-) conductors brownmillerites Sr(Fe,Co)O\(_2\).\(^{173}\) and Nd\(_2\)NiO\(_4\)-\(\delta\)\(^{174}\) (Figure 5.1a and 5.1c). In one recent study on O\(^2\-) conductor Nd\(_2\)NiO\(_4\)-\(\delta\) the low energy peaks in the phonon DOS was shown to vary as a function of the excess oxygen content \(\delta\). This should be compared and contrast with our finding that the phonon DOS of Li\(_{3+x}\)P\(_{1-x}\)Ge\(_x\)O\(_4\) (\(x = 0, 0.2, 0.4, 0.6, 0.8\) and 1) broadens upon increasing Li content without any significant shift in frequencies (expect the high-energy part of the spectrum that shift to lower frequency upon increasing Ge content but this is mainly due to the higher mass of Ge compared to P). Another interesting experimental result is about the copper sulfide (Cu\(_{2-x}\)Se) with superionic Cu\(^+\) conductivity at room temperature and which is known to have low-energy phonon DOS and lattice thermal conductivity.\(^{175}\) Phonon DOS of this materials are shown in Figure 5.1b and 5.1d at different temperatures.\(^{176}\) This specific broadening of some phonon peaks in the DOS immediately remind us of the same phenomena found in Li-conductor Li\(_3\)PS\(_4\). These previous studies strongly suggest that lattice dynamics and ionic conductivity are strongly inter-related. It will be very interesting 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.

5.2 Issue with Olivine compounds as Li-ion conductors

In the discussion of the trade-off between ionic conductivity and stability, we have noted that Olivine compounds seem to buck this trade-off have both small migration barrier and good stability against oxidation at relatively high voltage. We explained this peculiar behavior by the fact that Olivines exhibit low lithium band centers and migration barriers comparable to that of LISICON thiophosphates but high anion band centers comparable to those of LISICON phosphates. These characteristics make Olivine particularly interesting as a solid-state Li-ion conductor. Unfortunately, the one-dimensional nature of diffusion pathway in the olivine structure
Li-ions are omitted in these figures as they are represented by their density distribution. The zig-zag one-dimensional diffusion pathway of Lithium is clearly evident.

makes it prone to anti-site defects which can result in an apparent activation energy much higher than the intrinsic migration barrier. For example, the long-range diffusion barrier measured by EIS for LiMgPO$_4$ is 0.7-1.0 eV in previous work$^{13}$ and also in this study, much higher than the intrinsic migration barrier (~0.3 eV). We also observed this anti-site defect in our classical MD simulation of Li$_{0.8}$Sc$_{0.2}$Mg$_{0.8}$PO$_4$. The structure was generated by randomly replacing some Mg$^{2+}$ by Sc$^{3+}$. To compensate for the charge, some Lithiums were removed from the lattice creating Li vacancies along the diffusion channels. No anti-site defect is present in the initial structure. We ran the simulation at 1000K for ~100 ps. The Lithiums trajectory are shown in Figure 5.2 as the iso-surface of Li-ion probability distribution. Lithium ions diffuse in ‘zig-zag’ manner along the diffusion channel as expected. However, as we lower the value of the iso-surface probability, we found that there are some inter-channel crossings of Li, i.e. the diffusion is not strictly one-dimensional. This inter-channel crossing can be seen even more clearly when viewed along the diffusion pathway (b-axis) (Figure 5.3b). Lithium can be seen to pass through the position of Mg/Sc which implies that there are some vacancies at these locations since two ions cannot occupy the same crystallographic site at the same time. However, in the initial structure generated, there was no vacancy on Mg/Sc positions which raises the question of where Mg/Sc go to. The answer can be
Figure 5.3 a) and b) Isosurface of Li-ions probability distribution in olivine Li$_{1.2}$Sc$_{0.2}$Mg$_{0.8}$PO$_4$ at 1000K viewed along the diffusion pathway (b-axis). It can be seen from b) that there is a small probability of inter-channel diffusion via the position of Mg-ions. c) and d) Isosurface of Mg-ions probability distribution in olivine Li$_{1.2}$Sc$_{0.2}$Mg$_{0.8}$PO$_4$ at 1000K viewed along the diffusion pathway of Lithium (b-axis). Mg-ions are omitted in these figures as they are represented by their density distribution. It is clear from d) that some Mg-ions move into the Li-ion diffusion channel creating the anti-site defects that block the channel.

found by examining the Mg-ions trajectories shown in Figure 5.3c and 5.3d as the iso-surface of Mg-ion probability distribution. It is clear from Figure 5.3d that some Mg vacancies are thermally generated by the migration of Mg into the Li diffusion channels, creating effectively anti-site
defects that were also found in the experiments from XRD. Therefore, further studies are needed to increase the long-range ion conductivity of these Olivines by reducing anti-site defects using smaller particle sizes and/or having Li-excess in the lattice, which would potentially lead to the development of lithium superionic conductors with high stability against electrochemical oxidation.

5.3 High-throughput computation of phonon DOS and stability of Li-ion conductors

The study of lattice dynamics presents in this thesis relies heavily on phonon DOS which are not easy to get experimentally or computationally. Experimentally, the measurement of phonon DOS requires a neutron source which is available at only a few facilities around the world. Moreover, due to the relatively weak intensity of neutron beam (compared to synchrotron x-ray) and the inherently weak signals of inelastic scattering (compared to elastic scattering), a large amount of material (a few grams) and a long exposure time to neutron beam (a few hours) is required to obtain a good signal-to-noise ratio. Computationally, each phonon calculation requires a supercell which can have up to a few hundreds of atoms. Since DFT scales as number of atom to the cube, the calculation can become extremely expensive very quickly. Moreover, in the finite displacement approach, for each material, several configurations, in which some atoms are displaced from their equilibrium positions, are generated and the force computed. Symmetry of the crystal can be used to reduce the number of configurations needed. However, for compounds with low symmetry (especially structures with defects), the number of configurations generated can be several hundreds. This makes accurate phonon DOS calculations within DFT a highly non-trivial task and a high-throughput calculation very challenging although recent effort along this line has shown promising results.177 Nevertheless, in the short and medium term, since we are only interested in the phonon band center, we believe that a more accessible approach would be to compute phonon with a less accurate but computationally more efficient methods. One of these approach uses machine-learning based algorithm to fit lattice dynamics related quantities such as vibration entropy, heat capacity, average phonon frequency,.... with a (limited) database of DFT computed phonon.169 Another approach that we are pursuing as the follow-up of this thesis is based on more physical principles underlying phonon calculation.178 The main advantage of this method
Figure 5.4 Comparison between computed phonon band center using DFT from the whole Brillouin zone and only at the Γ-point for a) Total c) Anion and e) Li band centers. Comparison between DFT and approximated method band centers for b) Total d) Anion and f) Li band centers. Is that it doesn't require a supercell and needs only two single-point DFT calculations, independent
of the symmetry and how many atoms you have in the unit cell, unlike the exact DFT approach in which the number of configurations can explode very quickly for low-symmetry structure with many atoms in the unit cell. The main drawback is that only phonon at \( \Gamma \)-point can be computed within this approach.

The comparison between the phonon band centers computed with DFT using the full Brillouin zone and only \( \Gamma \)-point are shown in Figure 5.4a, 5.4c and 5.4e respectively for total, anion and Lithium band centers. We can see that as far we are interested only in the band center, phonon at \( \Gamma \)-point give excellent agreement with the exact calculations suggesting the dispersion in phonon band somehow smooths out while integrated over the entire energy range. Also shown in Figure 5.4 in the 2\(^{nd}\) column are the comparisons between \( \Gamma \)-point only DFT phonon band center and the one computed with the approximation mentioned earlier. The agreement for the total and anion band center is reasonable. However, the accuracy for Li band center is not enough. The reason behind this discrepancy is not fully understood at the moment but is likely due to the poor approximation in the eigenvectors used to compute the projected Li-band center. We think that these results can be improved by adding more configuration whose forces are computed with DFT and is currently under development. Once we achieve sufficient accuracy, a high-throughput calculation of phonon band center will be carried out and used to screen for ionic conductivity using the descriptor developed in this thesis.

The high-throughput calculation of the oxidation and reduction potential using the method outline in chapter 3 is more straightforward. Using the Materials Project database, we have screened for all Lithium containing compounds whose energy above hull is smaller than 20 meV per atom, bandgap smaller than 0.5 eV (to avoid electronic conductivity) and excluding transition metals V, Cr, Mn, Fe, Co, Ni, Cu, Re, Os, Ir, Pt and Au. Moreover, we include only ternary and quaternary compounds. Using these criteria, we have selected 931 compounds whose computed oxidation and reduction voltage are shown in Figure 5.5 grouped according to the chemistry of their anions (oxides, sulfides, halides, pnictides and hydrides). Several observations can be made. First of all, fluorides have the highest oxidation potentials, higher that oxides as expected. Second, sulfides and hydrides tend to have low oxidation potential. The same is true for nitrides, however, one particularity of nitrides is that many of them are stable against reduction by Lithium which make them particularly attractive as possible solid-state electrolytes for Li-ion battery. Moreover,
we note that while oxidation potential tends to be determined by the chemistry of the anions framework, the reduction potential varies widely even within a given chemistry. One of the objective of the follow-up study will be the rationalization of the observed variation in oxidation and reduction potential based on lattice dynamics related properties such as anion band centers which was shown to correlate well with the oxidation potential in Lisicon and Olivine families. The final goal would be to include more chemistries and structures into consideration and proposes a more universal descriptor for stability.

In addition to the decomposition potential, we also have at our disposition the decomposition products from the oxidation and reduction of the electrolytes. We can analyze these
Figure 5.6 Decomposition products from the oxidation (1st row) and reduction (2nd row) of Li-ion conductors of oxides and halides and sulfides grouped according to whether they are unary, binary or ternary compounds (with or without Lithium)

decompositions product in an attempt to 'design' the solid electrolyte interfaces that are stable, ionically conductive but electronically insulating. In Figure 5.6, we show the distribution of the decomposition products oxides, halides and sulfides. In general, one wants to avoid unary materials since they tend to be metallic and therefore conduct electron. We also want to avoid binary compounds because most of them don’t conduct Li very well. This simple analysis can be made much more sophisticated by for example including other metric such as elasticity, mechanical and thermal properties and optimize these decomposition products to have the desired properties.

5.4 Meyer-Neldel Rule in Lithium conducting polymers

In last section of chapter 4, we have shown that the Meyer-Neldel rule applies to a wide range of Li-ion conductors and we explained this behavior by invoking the linear relationship between the entropy of migration and the migration barrier or enthalpy of migration and justify
Figure 5.7 Meyer-Neldel behavior reported for several Li-conducting polymer electrolytes. It is remarkable that the correlation also exists in polymer whose temperature-dependent ionic conductivity is not of Arrhenius type.\textsuperscript{180}

this relation within the multi-excitation entropy theory. Moreover, our quantitative derivation of Meyer-Neldel rule relies critically on the Arrhenius equation and microscopic model of diffusion. It is therefore very intriguing to see that Meyer-Neldel rule or compensation law was also reported in the Li-conducting polymer\textsuperscript{180} (Figure 5.7) where the ionic conductivity is not governed by Arrhenius equation but the so-called Vogel-Tamman-Fulcher equation\textsuperscript{32,33}:

\[
\sigma = \frac{A}{\sqrt{T}} \exp \left( -\frac{E_a}{k_B(T - T_g)} \right)
\]  
(5.1)
Where \( T_g \) is identified with the glass transition temperature of the polymer although in practice it has been found that its values are different from the \( T_g \) obtained from calorimetry. While we have a relatively satisfactory understanding of Meyer-Neldel rule for crystalline materials, to the best of our knowledge, there is no detail explanation of this behavior in polymeric systems. One of the main difficulty is the absence of microscopic model of Li diffusion in polymer. Because of this, we don’t know what are the physical parameters that go into the pre-exponential factor \( A \), although it is believe that it contains the concentration of mobile species. Moreover, in crystalline materials, the intercept of the Meyer-Neldel plot is related to the Gibbs free energy of defect formation. It is therefore natural to ask whether the same conclusion also applies to Lithium conducting polymers. Finally, the exact nature of \( T_g \) is not well understood. In particular, it would be interesting to see if there exists any Meyer-Neldel type behavior that involves \( T_g \). We believe that understanding this correlation in polymers is not only relevant from a pure scientific perspective but might also be of practical interest as it can lead to new strategies to increase the ionic conductivity in polymer systems.\(^{181}\)
Appendix

A. Computation of phonon DOS and migration barrier

A.1 Density Functional Theory calculations

For computations, we used Density functional theory based on the Perdew–Burke–Ernzerhof (PBE)\textsuperscript{182} generalized gradient approximation as implemented in the VASP package.\textsuperscript{183} The core electrons were treated within the Projector Augmented Wave (PAW) method.\textsuperscript{184} Migration barriers for a lithium ion hopping were calculated using the climbing-image nudged elastic band method\textsuperscript{135} in a 2x2x1 supercell for LISICON (space group Pnma) while for the LISICON (space group Pnm2\textsubscript{1}), a 2x2x2 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 meV for phonon DOS calculations but haven’t found any significant change (Fig. S1) indicating that phonon DOS calculations are already well converged at 520 meV 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

\[
\begin{array}{c}
\text{Li}_3\text{PO}_4 \\
\text{Pnma}
\end{array}
\begin{array}{c}
\text{Li}_3\text{VO}_4 \\
\text{Pmn2}_1
\end{array}
\begin{array}{c}
\text{Li}_3\text{PS}_4 \\
\text{Pmn2}_1
\end{array}
\begin{array}{c}
\text{LiMgPO}_4 \\
\text{Pnma}
\end{array}
\begin{array}{c}
\text{LiInGeO}_4 \\
\text{Pnma}
\end{array}
\]

\[
\begin{array}{c}
\text{Li}_3\text{PO}_4 \\
\text{Pnma}
\end{array}
\begin{array}{c}
\text{Li}_3\text{VO}_4 \\
\text{Pmn2}_1
\end{array}
\begin{array}{c}
\text{Li}_3\text{PS}_4 \\
\text{Pmn2}_1
\end{array}
\begin{array}{c}
\text{LiMgPO}_4 \\
\text{Pnma}
\end{array}
\begin{array}{c}
\text{LiInGeO}_4 \\
\text{Pnma}
\end{array}
\]

Figure A.1 Comparison of a) computed Li-band center and b) computed total band center of some representative compounds in Lisicon and Olivine families using different functional and different cut-off energies for plane wave basis set.
DOS to higher frequencies resulting in an upward shift of band center (Figure A.1) in agreement with previous study. 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. For the calculations of migration barrier using NEB, our results compare very well with the previously published work. Computed migration barriers of Olivines studied here such as LiMgPO₄ are comparable to those of other Olivine materials such as LiMPO₄ (M=Mn, Fe, Co and Ni, 0.1-0.4 eV) and LiMXO₄ (main group M²⁺-X⁵⁺, M²⁺-X⁵⁺; M=Mg, Ca, Sr, Ba, Sc, Y, Al, In, Ga and rare-earth elements; X=Si, Ge, Sn, P, As and Sb). These good agreements further support that our results are well-converged with respect to all relevant parameters (K-point mesh, cut-off energy for plane wave basis set, number of images...).

![Figure A.2](image_url)

**Figure A.2** Mean square displacement (MSD) as a function of time. MSD increases linearly with time with the slope proportional to the diffusion coefficient.
A.2 Classical Molecular Dynamics Calculations

Classical molecular dynamics (MD) simulations were performed using LAMMPS package.\textsuperscript{188} The interatomic potential used in this work were published elsewhere\textsuperscript{189,190} and was shown to give good accuracy on chemically similar system.\textsuperscript{153,154} The potential contains three terms: A Coulomb term to account for the long-range interaction between ions, a Morse term for the short-range repulsive interaction and a $r^{-6}$ term which was found to be important to accurately model the system especially in the high-temperature regime by making the repulsive interaction ‘harder’. We used a 4x4x2 supercell of Li$_3$VO$_4$ and Li$_3$PO$_4$ (Pnma) and a 4x4x4 supercell of Li$_4$GeO$_4$ containing respectively 1024 and 1152 atoms. We also simulated non-stoichiometric compositions Li$_{3+x}$V$_{1-x}$Ge$_x$O$_4$ (x = 0.2, 0.4, 0.6 and 0.8) by randomly replacing V by Ge in the supercell and introducing interstitial lithium to make the whole supercell electrically neutral. The supercells were relaxed until the forces on the ions fall below $10^{-6}$ eV/Å. The MD simulations were performed in NVT ensemble using Nose-Hoover thermostat to control the temperature while the volumes of the unit cells were fixed at their experimental values. A step of 2 fs was used and the simulations were performed for at least 100 ps. From the MD trajectory, the mean-square displacements (MSD) of different ions can be computed. The (self) diffusion coefficient was extracted from the slope of the MSD versus time and the ionic conductivity was computed using the Nernst-Einstein relation. The Li-ion density and Van-Hove correlation function were computed from the MD trajectories using the pymatgen\_diffusion module\textsuperscript{155} in the Pymatgen package.\textsuperscript{191}
B. Phonon DOS measurements

B.1 Phonon DOS extractions

All phonon DOS were measured at the Wide Angular-Range Chopper Spectrometer (ARCS) beamline at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (Figure B.1). The beamline is equipped with a large solid angle of detector coverage made of a
massive array of He\textsuperscript{3} linear position sensitive detectors. The spectrometer at ARCS covers the entire spectrum of neutron energy from cold to hot neutron allowing the studies of a variety of physical/chemical phenomena in condensed matters characterizing by excitation energy ranging from a few to several hundred meV.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{The scattering function $S(Q,E)$ of Li\textsubscript{3}PO\textsubscript{4}. The intense red feature around 0 energy transfer are elastic peaks (diffraction) which have to be remove when converting $S(Q,E)$ in the phonon DOS.}
\end{figure}

Approximately 5g 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.\textsuperscript{193} The partial differential cross
section was measured via time-of-flight spectroscopy and is directly proportional to the scattering
function \( S(Q,E) \).\textsuperscript{194} The partial differential cross section and scattering function \( S(Q,E) \) are the raw
data and are directly proportional to neutron count recorded by the detector. An example of
scattering function of Li\(_3\)PO\(_4\) is shown in Figure B.2. The x-axis is the magnitude of the wavevector
\( Q \) and the y-axis is the energy transfer. We use the magnitude of \( Q \) instead the vector \( Q \) because
our sample is a powder. The intense feature around 0 energy transfer correspond to elastic
scattering which is nothing the neutron diffraction pattern of crystal. These elastic peaks have to
be removed during the data extraction process. The phonon DOS was extracted from the positive
energy transfer part of the \( S(Q,E) \) which corresponds to energy loss by neutron to the crystal
(inelastic scattering). The phonon DOS extraction involves choosing several parameters such as
background fraction (the typical value of this parameter is 1), constant fraction (the value of this
parameter is chosen such that the intensity above the highest frequency is as close to zero as
possible), the cutoff (this parameter is used to remove the elastic peak near the origin), eStop (the
energy cutoff above which the intensity is set to zero, its values depend on the highest frequency
of the material and can be guessed reliably from the spectra), the range of \( Q \) over which the
integration will be performed, etc. The sensitivity of the extracted DOS to these parameters are
shown in Figure B.3. For each plot we fix all the parameters except one, which was varied
systematically to examine its influence on the reduced data. 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 Å\(^{-1}\). For sulfides, the parameters were the same except the range of wave vectors
used was from 4-9 Å\(^{-1}\).
Figure B.3 Sensitivity of phonon density-of-states to reduction parameters for Li$_3$PO$_4$ Pnma at 10 K. a) Background fraction, b) constant fraction. c) Cutoff. d) elasticutAvg. e) eStop. f) longE.
Figure B.3 Sensitivity of phonon density-of-states to reduction parameters for Li$_3$PO$_4$ Pnma at 10 K. g) Range in the magnitude of the wave vector ($q_{\text{min}}$-$q_{\text{max}}$) in Å$^{-1}$, over which we integrate the scattering function to generate the DOS. h) Order of multiphonon correction N. i) Tolerance.

B.2 Measured phonon DOS

Here we give all the measured phonon DOS which are not shown in Chapter 3. Unless otherwise stated, the detail of experimental conditions and data extraction are the same and detailed in previous sections. For Li$_3$PO$_4$ (Pmn21), we found that there is some water contamination of the sample. It was difficult to remove all of the water from the sample, which resulted in a large background scattering. This is the cause for the intensity to be nonzero $\sim$100 meV. A higher constant fraction (0.8) during analysis of the sample was used.
**Top Diagram:**
- **Compound:** Li$_4$GeO$_4$
- **Symmetry:** Cmcm
- **Temperature:** 100 K

**Bottom Diagram:**
- **Compound:** Li$_3$PO$_4$
- **Symmetry:** Pmn2$_1$
- **Temperature:** 100 K
Li₃AsO₄ Pnma

Compared

100 K

LiMgPO₄ Pnma

Compared

100 K
$\text{Li}_{3.4}\text{Ge}_{0.4}\text{P}_{0.6}\text{S}_4$ P42/nmc

Intensity (Arb. Unit)

Energy (meV)

100 K
C. Material synthesis and characterizations

C.1 Synthesis of oxide compounds

For neutron inelastic scattering measurements, the materials were synthesized through solid-state synthesis methods. Appropriate mixtures (5-10% excess lithium for Li₃PO₄, Li₄GeO₄, Li₃.₄Ge₀.₄Po.₆O₄, Li₃.₆Ge₀.₆V₀.₄O₄, and Li₃.₈Ge₀.₈V₂O₄, and stoichiometric mixtures in all other cases) of Li₂CO₃ (99.998% Alfa Aesar), (NH₄)₂HPO₄ (98% Strem Chemicals), V₂O₅ (>99.6% trace metal basis, Aldrich), GeO₂ (>99.99% trace metal basis, Aldrich), and MgO (99.95%, Alfa Aesar) were ground with a mortar and pestle or mixed overnight in ethanol. The resulting powders were calcined in dry air at 800 °C for 20 hours (10 hours for Li₄GeO₄, Li₃VO₄, and Li₃PO₄) using a ramp rate of 5 °C/min on heating and cooling to produce the desired material. Li₃PO₄ (Pmn2₁) was obtained from Sigma Aldrich and was heated under vacuum to remove moisture before use. Appropriate mixtures (5% excess Li for Li₃PO₄ and Li₃.₂Ge₀.₂Po.₈O₄, and stoichiometric mixtures in all other cases) of Li₂CO₃ (99.998% Alfa Aesar), (NH₄)₂HPO₄ (98% Strem Chemicals), V₂O₅ (>99.6% trace metal basis, Aldrich) and GeO₂ (>99.99% trace metal basis, Aldrich) were ground with a mortar and pestle. The resulting powders were calcined in dry air at 800 °C for 10 hrs using a ramp rate of 5 °C/min to produce the desired material. These powders were pressed at 1 GPa into pellets with a 6 mm diameter and were approximately 1-1.5 mm thick. The pellets were then sintered at 800 °C for 10 hrs using a ramp rate of 5 °C/min for cooling and heating, and then were polished before being sputtered with 100 nm of gold on each face of the pellet. Lithium phosphate doped with 40% lithium vanadate required an additional calcination at 900 °C to achieve a solid solution of lithium vanadate and lithium phosphate, before the powders were sintered at the previously described sintering conditions.

C.2 Synthesis of sulfide compounds

Synthesis preparation steps of sulfur-based conductors were performed under an argon atmosphere. The starting materials used for the synthesis of γ-Li₃PS₄ (Pmn2₁) consisted of Li₂S (>99% purity, Mitsuwa Chemical) and P₂S₅ (>99% purity, Sigma Aldrich). These reagents were weighted in the appropriate molar ratio and mixed by planetary ball milling for 20 h. The specimens were then pressed into pellets, sealed in a quartz tube at 10 Pa, and heated at 500 °C for 8 h, which was slowly cooled to room temperature. For β-Li₃PS₄ (Pnma) the Li₂S powder was
Figure C.1 X-ray diffraction patterns of LISICON solid solutions of Li$_{3+x}$P$_{1-x}$Ge$_x$O$_4$, Li$_{3+x}$V$_{1-x}$Ge$_x$O$_4$ and Li$_3$P$_{1-x}$V$_x$O$_4$ ($x = 0$, 0.2, 0.4, 0.6, 0.8 and 1). All the compounds crystallize into $Pnma$ space group with the exception of Li$_3$VO$_4$ and Li$_3$V$_{0.8}$P$_{0.2}$O$_4$ which have $Pmn2_1$ space group and Li$_4$GeO$_4$ which crystallize in the $Cmcm$ space group.

milled to obtain fine particles using a ball-milling apparatus. All of the procedures were conducted
Figure C.2 XRD spectra of all compound measured in this study. Most samples were phase pure, impurity peaks are identified with an asterisk (*). a) XRD spectra of Li$_4$SnS$_4$, Li$_4$GeS$_4$, Li$_3$PS$_4$, LiMgPO$_4$ and Li$_3$AsO$_4$. For Li$_4$SnS$_4$ and Li$_4$GeS$_4$, amorphous hump at low angles is from the plastic dome of the sealed cell that is used to measure the reactive sulfides. The main impurity phase in Li$_3$PS$_4$ is Li$_2$PS$_3$ b) Diffraction pattern for Li$_{4-x}$Ge$_{1-x}$P$_x$S$_4$ compared to reference patterns. Labels of solid solution have the percentage of vanadium noted (V20 corresponds to x=0.2). c) Diffraction pattern for Li$_{4-x}$Ge$_{1-x}$P$_x$S$_4$. For phonon DOS measurements, for Li$_3$PS$_4$ (Pmn2$_1$) sample 1 and 2 were mixed, and for Li$_{3.25}$Ge$_{0.25}$P$_{0.75}$S$_4$ (Pnma) samples 1 – 3 were mixed. Minute Li$_2$PS$_3$ impurity can be found in Li$_3$PS$_4$ samples.

under an argon atmosphere. Starting materials were weighed in the appropriate molar ratio and mixed by planetary ball milling for 40 h. The samples were then pressed into pellets, sealed in a quartz tube at 10 Pa, and heated at 300 °C for 8 h, which was cooled slowly to room temperature. For Li$_{4-x}$Ge$_{1-x}$P$_x$S$_4$ (x = 0.75, Pnma) the starting materials used for the synthesis were Li$_2$S (>99% purity, Mitsuwa Chemical) and P$_2$S$_5$ (>99% purity, Sigma Aldrich), and GeS$_2$ (>99.99% purity, Kojundo Chemical Laboratory). These powder samples were weighed in the appropriate molar
ratio and mixed for 30 min using a vibrating mill (CMT, TI-100). The samples were then pressed into pellets, placed into a carbon crucible, and then sealed at 10 Pa in a carbon-coated quartz tube. After being heated at a reaction temperature of 750 °C for 8 h, which was quenched subsequently in ice water. Li$_3$Ge$_{0.4}$S$_{0.6}$S$_4$ (P4$_2$/nmc) was prepared according to previous work. Li$_4$GeS$_4$ was synthesized by reacting stoichiometric ratios of Li$_2$S (Alfa Aesar 99.9% metal basis) and GeS$_2$ (Santa Cruz Biotechnology) at 700 °C for 8 h followed by a 12-hour cooling to room temperature under argon. Li$_3$SnS$_4$ was synthesized by reacting stoichiometric ratios of Li$_2$S (Alfa Aesar 99.9% metal basis) and SnS$_2$ (Santa Cruz Biotechnology) at 700 °C for 8 h followed by a 12-hour cooling to room temperature under argon. Li$_{3.33}$Sn$_{0.33}$P$_{0.67}$S$_4$ (P4$_2$/nmc, NEI Corporation) was used as purchased.

Table C.1 Atomic ratios between cations in solid solutions of Li$_3$P$_{1-x}$V$_x$O$_4$, Li$_3$Ge$_{1-x}$V$_x$O$_4$ and Li$_3+x$P$_{1-x}$Ge$_x$O$_4$ (x = 0, 0.2, 0.4, 0.6, 0.8 and 1) measured from inductively couple plasma-atomic emission spectroscopy. Theoretical, measured, and percent difference in cation ratios are shown, with positive values of the percent difference representing excess of the measured ratio to the theoretical ratio.$^{195}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Theoretical Ratios</th>
<th>Measured Ratios</th>
<th>Percent Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Li/(P+Ge+V)</td>
<td>P/Ge Ge/V P/V</td>
<td>Li/(P+Ge+V)</td>
</tr>
<tr>
<td>Li$_3$PO$_4$</td>
<td>3.00</td>
<td>2.92</td>
<td></td>
</tr>
<tr>
<td>Li$<em>3$Ge$</em>{0.8}$P$_{0.2}$O$_4$</td>
<td>3.20</td>
<td>4.00</td>
<td>2.35 4.13 -3%</td>
</tr>
<tr>
<td>Li$<em>3$Ge$</em>{0.6}$P$_{0.4}$O$_4$</td>
<td>3.40</td>
<td>1.50</td>
<td>3.35 1.50 -2% 0%</td>
</tr>
<tr>
<td>Li$<em>3$Ge$</em>{0.6}$P$_{0.4}$O$_4$</td>
<td>3.60</td>
<td>0.67</td>
<td>3.45 0.67 -4% 1%</td>
</tr>
<tr>
<td>Li$<em>3$Ge$</em>{0.8}$P$_{0.2}$O$_4$</td>
<td>3.80</td>
<td>0.25</td>
<td>3.56 0.25 -6% -1%</td>
</tr>
<tr>
<td>Li$_3$GeO$_4$</td>
<td>4.00</td>
<td>3.81</td>
<td></td>
</tr>
<tr>
<td>Li$<em>3$Ge$</em>{0.8}$V$_{0.2}$O$_4$</td>
<td>3.80</td>
<td>4.00</td>
<td>3.57 4.16 -6% 4%</td>
</tr>
<tr>
<td>Li$<em>3$Ge$</em>{0.6}$V$_{0.4}$O$_4$</td>
<td>3.60</td>
<td>1.50</td>
<td>3.45 1.53 -4% 2%</td>
</tr>
<tr>
<td>Li$<em>3$Ge$</em>{0.4}$V$_{0.6}$O$_4$</td>
<td>3.40</td>
<td>0.67</td>
<td>3.33 0.66 -2% -2%</td>
</tr>
<tr>
<td>Li$<em>3$Ge$</em>{0.2}$V$_{0.8}$O$_4$</td>
<td>3.20</td>
<td>0.25</td>
<td>3.19 0.26 0% 5%</td>
</tr>
<tr>
<td>Li$_3$VO$_4$</td>
<td>3.00</td>
<td>3.00</td>
<td></td>
</tr>
<tr>
<td>Li$<em>3$V$</em>{0.8}$P$_{0.2}$O$_4$</td>
<td>3.00</td>
<td>4.00</td>
<td>2.93 4.22 -2% 5%</td>
</tr>
<tr>
<td>Li$<em>3$V$</em>{0.6}$P$_{0.4}$O$_4$</td>
<td>3.00</td>
<td>1.50</td>
<td>2.89 1.61 -4% 7%</td>
</tr>
<tr>
<td>Li$<em>3$V$</em>{0.4}$P$_{0.6}$O$_4$</td>
<td>3.00</td>
<td>0.67</td>
<td>2.96 0.71 -1% 6%</td>
</tr>
<tr>
<td>Li$<em>3$V$</em>{0.2}$P$_{0.8}$O$_4$</td>
<td>3.00</td>
<td>0.25</td>
<td>2.98 0.26 -1% 5%</td>
</tr>
</tbody>
</table>

C.3 Material characterizations

The phase purity of LISICON sintered pellet samples were performed using X-ray diffraction on a Panalytical X’Pert Pro diffractometer with Cu Kα radiation with one-hour
continuous scans from 15-80 degrees 2θ (Figure C.1). Lattice parameters of all samples were refined using profile matching of Fullprof based on space group $Pnma$ except $Pmn2_1$ for $Li_3VO_4$ and $Li_3V_{0.8}P_{0.2}O_4$ having symmetry, and $Cmcm$ for $Li_4GeO_4$ (Table S2). Pseudo-Voigt function was used for peak shape to refine the peak positions in order to determine the lattice parameters. The atomic positions and occupancy were not refined. For thio-Lisicon, phase purity was confirmed by X-ray diffraction (Figure C.2) measured on a Panalytical X'Pert Pro, Rigaku Smartlab, or Rigaku MiniFlex300 diffractometers with Cu k-alpha sources. All sulfur-based samples were stored under inert atmosphere until immediately before measuring the phonon density of states at Oak Ridge National Laboratory. Elemental analyses of cations were determined using inductively coupled plasma-optical emission spectroscopy (ICP-AES) with an Agilent 5100 ICP-AES, which showed a good agreement with targeted stoichiometries (Table S3). Samples and references were dissolved in nitric acid to be measured. The porosity of sintered pellets was determined by measurement with a micrometer, which was consistent with scanning electron microscope (SEM) secondary electron images of fractured cross-sections of pellets on a Zeiss Merlin SEM.
D. EIS measurements of ionic conductivity

Pellets were sputtered with 100 nm of gold on each face and were generally stored within an argon-filled glove box to avoid reactions with water and carbon dioxide. Electrochemical impedance spectroscopy (EIS) data were collected from gold sputtered pellets assembled between two stainless steel current collectors with Biologic potentiostats with VSP300 boards. Data were collected between 7 MHz and 0.1 Hz using an AC voltage amplitude of 10 mV and 1 V to increase the signal to noise ratio for measurements of highly resistive samples. The temperature of EIS measurements was controlled with an Espec SJ-241 environmental chamber between -30 °C and 150 °C. Impedance spectra were fit to the equivalent circuit using Z-fit within EC-Lab from BioLogic, from which the extracted high-frequency circle resistance was used to compute lithium ion resistivity as a function of temperature. Impedance results were fitted with resistance and constant-phase elements (Q) as \( R_{\text{series}} + \frac{R_{\text{bulk}}}{Q_{\text{bulk}}} + Q_{\text{elec}} \) for results with one distinct semi-circle using the equivalent circuit (Figure D.1) and \( R_{\text{series}} + \frac{R_{\text{bulk}}}{Q_{\text{bulk}}} + \frac{R_{\text{gb}}}{Q_{\text{gb}}} + Q_{\text{elec}} \) for two distinct semicircles using the equivalent circuit (Figure D.2). \( R_{\text{series}} \) represents the resistance of the leads and cell, \( Q_{\text{elec}} \) represents the imperfect capacitance of the planar electrode surface at low frequencies, \( \frac{R_{\text{bulk}}}{Q_{\text{bulk}}} \) represent the parallel resistance and capacitance of the bulk material, and \( \frac{R_{\text{gb}}}{Q_{\text{gb}}} \) represents the parallel resistance and capacitance of the grain boundaries.

Figure D.1 Equivalent circuit used to extract the value of resistance from EIS spectra with a) one semi-circle, b) two semi-circle. The conductivity is computed from the resistance using the formula: Conductivity = Thickness/(Area*Resistance).

For LISICONs without partial lithium occupancy (Li\(_3\)P\(_{1-x}\)V\(_x\)O\(_4\) (x = 0, 0.2, 0.4, 0.6, 0.8 and 1) and Li\(_4\)GeO\(_4\)), the impedances were measured over the temperature range 90 °C to 150 °C (below 90 °C the resistances were too high). For compounds with partial lithium occupancy (Li\(_{3+x}\)V\(_{1-x}\)Ge\(_x\)O\(_4\) and Li\(_{3+x}\)P\(_{1-x}\)Ge\(_x\)O\(_4\) (x = 0.2, 0.4, 0.6 and 0.8)), the impedances were measured over the temperature range -30 °C to 150 °C. LISICONs without partial lithium occupancy exhibited only one semicircle.
Figure D.2 Nyquist impedance plots of a) Li$_3$PO$_4$, b) Li$_4$GeO$_4$, c) Li$_{3.2}$Ge$_{0.2}$V$_{0.8}$O$_4$, and d) Li$_{3.2}$Ge$_{0.2}$P$_{0.8}$O$_4$ at select temperatures. Two semicircles of Li$_{3.2}$Ge$_{0.2}$P$_{0.8}$O$_4$ found at low temperatures merged into one semicircle at temperatures greater than $30^\circ$C in Figure D.2d. The open circles are the collected data points while the lines joining the open circles correspond to the fits with the employed equivalent circuits.$^{195}$

While compounds with partial lithium occupancy exhibited two distinct semi-circles below $-30^\circ$C - $60^\circ$C which can be attributed to the bulk and grain boundary conductivity. Nyquist plots of selected compositions Li$_3$PO$_4$, Li$_4$GeO$_4$, Li$_{3.2}$Ge$_{0.2}$V$_{0.8}$O$_4$ and Li$_{3.2}$Ge$_{0.2}$P$_{0.8}$O$_4$ are shown in Figure 3a, 3b, 3c and 3d respectively. Two semicircles of Li$_{3.2}$Ge$_{0.2}$P$_{0.8}$O$_4$ found at low temperatures merged into one semicircle at temperatures greater than $30^\circ$C in Figure 3d. The high-frequency
Table D1. Capacitance and the ideality factor alpha of the constant phase element \((Q = 1/(Q_0(i\omega)^\alpha))\) at 105 °C for compounds without partial Li occupancy and 0 °C for compounds with partial Li occupancy.\(^{195}\)

<table>
<thead>
<tr>
<th></th>
<th>Total (F)</th>
<th>Alpha</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Li}_3\text{PO}_4)</td>
<td>1.683E-10</td>
<td>0.894</td>
</tr>
<tr>
<td>(\text{Li}_4\text{GeO}_4)</td>
<td>1.246E-10</td>
<td>0.961</td>
</tr>
<tr>
<td>(\text{Li}_3\text{VO}_4)</td>
<td>1.864E-10</td>
<td>0.889</td>
</tr>
<tr>
<td>(\text{Li}<em>3\text{V}</em>{0.2}\text{P}_{0.8}\text{O}_4)</td>
<td>1.816E-10</td>
<td>0.896</td>
</tr>
<tr>
<td>(\text{Li}<em>3\text{V}</em>{0.4}\text{P}_{0.6}\text{O}_4)</td>
<td>1.922E-10</td>
<td>0.884</td>
</tr>
<tr>
<td>(\text{Li}<em>3\text{V}</em>{0.6}\text{P}_{0.4}\text{O}_4)</td>
<td>1.974E-10</td>
<td>0.875</td>
</tr>
<tr>
<td>(\text{Li}<em>3\text{V}</em>{0.8}\text{P}_{0.2}\text{O}_4)</td>
<td>1.965E-10</td>
<td>0.873</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Bulk (F)</th>
<th>Alpha</th>
<th>Grain boundary (F)</th>
<th>Alpha</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Li}<em>{3.2}\text{Ge}</em>{0.2}\text{P}_{0.8}\text{O}_4)</td>
<td>1.113E-10</td>
<td>0.997</td>
<td>1.800E-09</td>
<td></td>
</tr>
<tr>
<td>(\text{Li}<em>{3.4}\text{Ge}</em>{0.4}\text{P}_{0.6}\text{O}_4)</td>
<td>1.134E-10</td>
<td>0.976</td>
<td>1.894E-09</td>
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</tr>
<tr>
<td>(\text{Li}<em>{3.6}\text{Ge}</em>{0.6}\text{P}_{0.4}\text{O}_4)</td>
<td>1.110E-10</td>
<td>1.000</td>
<td>3.540E-09</td>
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</tr>
<tr>
<td>(\text{Li}<em>{3.8}\text{Ge}</em>{0.8}\text{P}_{0.2}\text{O}_4)</td>
<td>1.330E-10</td>
<td>0.939</td>
<td>4.601E-09</td>
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</tr>
<tr>
<td>(\text{Li}<em>{3.8}\text{Ge}</em>{0.8}\text{V}_{0.2}\text{O}_4)</td>
<td>1.667E-10</td>
<td>0.926</td>
<td>7.970E-09</td>
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</tr>
<tr>
<td>(\text{Li}<em>{3.6}\text{Ge}</em>{0.6}\text{V}_{0.4}\text{O}_4)</td>
<td>1.101E-10</td>
<td>0.976</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Li}<em>{3.4}\text{Ge}</em>{0.4}\text{V}_{0.6}\text{O}_4)</td>
<td>1.221E-10</td>
<td>0.962</td>
<td>4.686E-09</td>
<td></td>
</tr>
<tr>
<td>(\text{Li}<em>{3.2}\text{Ge}</em>{0.2}\text{V}_{0.8}\text{O}_4)</td>
<td>1.211E-10</td>
<td>0.960</td>
<td>1.847E-08</td>
<td></td>
</tr>
</tbody>
</table>

The semicircle was attributed to bulk conduction, and the low-frequency semicircle was attributed to grain boundary conduction as reported previously.\(^{57}\) The ~45-degree tail at low frequencies was assigned to effects of the planar gold electrode surface. The capacitance as well as the ideality factor of the constant phase elements are shown in Table D1. For compounds with partial Li occupancy, the capacitance associated with the grain boundary is larger than that of the bulk as expected. For compounds without partial Li occupancy, only one semi-circle can be resolved, but based on their capacitances, we can conclude that the main contribution to this total capacitance come from the diffusion process that occurs in the bulk instead of the grain boundary.\(^{195}\)
E. Computed Phonon Density of States

E.1 Phonon DOS of stoichiometric compounds

Li₂CdGeO₄

Li₂CdGeS₄

Li₂CdGeSe₄

Li₂CdSiO₄

Li₄GeO₄

Li₄GeS₄
E.2 Phonon DOS of non-stoichiometric compounds

To compute the phonon DOS of non-stoichiometric compounds with partial occupancy is a significant challenge due to the presence of partial occupancy at various crystallographic sites as well as the reduction of symmetry caused by the introduction of impurities (dopants) into the lattice which results a drastic increase in the computational time. We found that, with a very good accuracy, we can approximate the Lithium band center of these heavily doped compounds by a linear combination of the Lithium band center of their end members (Figure E.1). For example, the Li band center of Li$_{3.25}$Ge$_{0.25}$P$_{0.75}$O$_4$ ($\omega_{LGPO25}$) can be approximated as:

$$\omega_{LGPO25} = 0.25 \times \omega_{LGO} + 0.75 \times \omega_{LPO}$$

where $\omega_{LGO}$ and $\omega_{LPO}$ are respectively the Li band center of Li$_4$GeO$_4$ and Li$_3$PO$_4$. We also show the comparison between the total and Li-projected phonon DOS of Li$_{3.25}$Ge$_{0.25}$P$_{0.75}$O$_4$, Li$_{3.75}$Ge$_{0.75}$V$_{0.25}$O$_4$, Li$_3$As$_{0.25}$P$_{0.75}$O$_4$ and Li$_{3.25}$Ge$_{0.25}$P$_{0.75}$S$_4$ computed directly with DFT and as the linear combination of the end members (Figure E.2 and E.3). Phonon DOS of these compounds along with the atom-projected phonon DOS are shown in Figure E.4.

![Figure E.1](image)

**Figure E.1** Comparison between the Li band center computed directly from phonon DOS of the doped compounds and the one obtained by the linear combination of the Li-band center of the end members.
Figure E.2 Comparison between the total phonon DOS of doped compounds with that of the end members and its linear combination.
Figure E.3 Comparison between the lithium phonon DOS of doped compounds with that of the end members and its linear combination.
Figure E.4 Computed phonon DOS of Li$_3$As$_{0.25}$P$_{0.75}$O$_4$, Li$_{3.25}$Ge$_{0.25}$P$_{0.75}$O$_4$, Li$_{3.25}$Ge$_{0.25}$P$_{0.75}$S$_4$ and Li$_{3.75}$Ge$_{0.75}$V$_{0.25}$O$_4$. 
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