2018

Characterization of lithium thiosilicophosphate glasses prepared by high energy ball milling

Mark Anthony Paul Aguilar
Iowa State University

Follow this and additional works at: https://lib.dr.iastate.edu/etd

Part of the Materials Science and Engineering Commons, and the Mechanics of Materials Commons

Recommended Citation
Aguilar, Mark Anthony Paul, "Characterization of lithium thiosilicophosphate glasses prepared by high energy ball milling" (2018).
Graduate Theses and Dissertations. 16502.
https://lib.dr.iastate.edu/etd/16502

This Thesis is brought to you for free and open access by the Iowa State University Capstones, Theses and Dissertations at Iowa State University Digital Repository. It has been accepted for inclusion in Graduate Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
Characterization of lithium thiosilicophosphate glasses prepared by high energy ball milling

by

Mark Anthony Paul Aguilar

A thesis submitted to the graduate faculty in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE

Major: Materials Science & Engineering

Program of Study Committee:
Steve W. Martin, Major Professor
Martin Thuo
Vincenzo Venditti

The student author and the program of study committee are solely responsible for the content of this thesis. The Graduate College will ensure this thesis is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University
Ames, Iowa
2018

Copyright © Mark Anthony Paul Aguilar, 2018. All rights reserved.
# TABLE OF CONTENTS

ABSTRACT ........................................................................................................... iii
CHAPTER 1 INTRODUCTION.................................................................................. 1
CHAPTER 2 BACKGROUND .................................................................................. 4

- 2.1 All Solid State Electrolyte ......................................................................... 4
- 2.2 Review Of A Lithium Ion Conducting Battery ........................................... 4
- 2.3 Dendrite Formation And Abuse Conditions ............................................. 5
- 2.4 Solid State Electrolytes ............................................................................. 8
- 2.5 Glass Structure ......................................................................................... 8
- 2.5 Silicon Sulfide And Phosphorus Sulfide SRO Structures .......................... 9
- 2.6 Mixed Glass Former Effect ..................................................................... 12
- 2.7 Electrolyte Materials ............................................................................... 13
- 2.8 Thermal Characteristic .......................................................................... 15
- 2.9 Mechanochemical Synthesis ................................................................... 15

CHAPTER 3 OBJECTIVES OF THE THESIS ....................................................... 17

CHAPTER 4 EXPERIMENTAL METHODS .......................................................... 19

- 4.1 Material Synthesis ................................................................................... 19
  - 4.1.1 SiS$_2$ Material Preparation ................................................................. 19
  - 4.1.2 Lithium Thiosilicophosphate Glasses ............................................... 20
- 4.2 Instrumentation ....................................................................................... 22
  - 4.2.1 Fourier Transform Infrared Spectroscopy .......................................... 22
  - 4.2.2 Raman Spectroscopy ....................................................................... 22
  - 4.2.3 Differential Scanning Calorimetry ...................................................... 23
  - 4.2.4 X-Ray Diffraction ............................................................................ 23
  - 4.2.5 Nuclear Magnetic Resonance ............................................................ 24

CHAPTER 5 RESULTS AND DISCUSSION ......................................................... 25

- 5.1 Structural Characterization ..................................................................... 25
  - 5.1.1 X-Ray Diffraction ............................................................................. 25
  - 5.1.2 Infrared Spectroscopy ...................................................................... 28
  - 5.1.3 Raman Spectroscopy ....................................................................... 30
  - 5.1.4 Nuclear Magnetic Resonance ............................................................ 38

- 5.2 Thermal Characterization ....................................................................... 45

CHAPTER 6 CONCLUSIONS AND FUTURE WORK ......................................... 48

BIBLIOGRAPHY ................................................................................................. 49

ACKNOWLEDGEMENTS .................................................................................. 55
ABSTRACT
An increasing demand for renewable energy has catalyzed investigations into improving battery technology. High energy density, longer cycling life, and safer battery materials are highly desirable. Research must go into developing advanced battery materials with properties designed for fast ionic conductivity, good chemical stability with the anode, and facile and low cost formability. Studying the short-range and intermediate-range atomic structures of materials will give insight into relationships between the atomic level structures of battery materials and their properties. In this research, the focus was upon developing new lithium ion conducting amorphous solid electrolytes in the compositional series \(0.6 \text{Li}_2\text{S} + 0.4[\text{xSiS}_2 + 1.5(1-x)\text{PS}_{5/2}]\) prepared via mechanochemical synthesis. These new amorphous solid electrolytes hold promise in improving the overall lithium battery performance by increasing the lithium ion conductivity and being electrochemically stable in contact with metallic lithium. In this work, these new lithium thiosilicophosphate amorphous solid electrolytes were characterized using Far/Mid Infrared (IR), Raman, and Nuclear Magnetic Resonance (NMR) spectroscopies, as well as X-Ray Diffraction (XRD) to determine their atomic level structures. Differential Scanning Calorimetry (DSC) was used to determine whether these planetary milled materials were in fact glassy in nature, which is having a thermal history consistent with one being formed from cooling a liquid, or whether they were just simply amorphous materials that would rapidly crystallize upon heating. The DSC measurements showed that these amorphous materials are
in fact glasses as they all exhibited a proper glass transition temperature, Tg, which indicates that these materials have sufficient internal thermal stability to access the supercooled liquid state above the Tg however below the crystallization temperature, Tc of the liquid. As a general trend, it was observed that the Tg increased as the phosphorous was replaced by silicon, that is with increasing x. The short range order (SRO) structures of these glasses, as determined by IR, Raman, and NMR spectroscopies, showed that the general trend for the compositional change of the SRO structural units was the expected P\(^1\) structures which were formed at x = 0, where the superscript 1 defines the number of bridging sulfurs (BS) on the P center, and upon addition of expected Si units, x > 0, the P\(^1\) units were extracted away to form ESi\(^2\) units and P\(^0\) SRO with no BS structures. In turn and required for charge compensation, the P\(^1\) SRO units upon losing this Li\(^+\) charge, were converted to edge sharing ESi\(^2\) possessing an additional BS structure. At the end of the compositional series as the P content decreases to zero, the Si SRO units necessarily convert back to Si\(^0\) units as required by the stoichiometry of the composition.
CHAPTER 1 INTRODUCTION

The high demand for portable electronics such as mobile phones, tablets, and laptops requires lightweight energy storage technology. Traditional portable energy storage relies on lithium ion conducting batteries found in the form of a lithium metal oxide (LiMO$_x$) like LiCoO$_2$, Li intercalated graphite cathode Li$_y$C, and liquid electrolyte (Demethyl carbonate/Ethylene Carbonate) containing LiPF$_6$ salt [1]. Although they provide a great way for energy storage, they suffer from a potential fire hazard associated with metallic lithium dendrite shorts across liquid electrolyte from the anode to cathode. To solve this problem, all solid state sulfide electrolyte separators have been investigated which provide a hard physical barrier between the anode and cathode and offer promise in preventing lithium dendrites from shorting across the electrodes [1-3]. For these reasons, all solid state batteries can improve the safety in commercial lithium metal oxide batteries.

As well as improving the safety of batteries, fast ionic conductivities are necessary to compete with conventional batteries. Sulfide and oxide based electrolyte-separators include Li$_{10}$Ge$_2$P$_2$S$_{12}$ with very high ionic conductivity of $10^{-2}$ S/cm at room temperature, one of the best ionic conductors to-date, La$_{0.5}$Li$_{0.5}$TiO$_3$, Li$_2$S-SiS$_2$-Li$_3$PO$_4$ also have good room temperature ionic conductivities of $10^{-3}$ S/cm [4-7]. Compounds containing lithium, silicon, and phosphorus may have promise to makes novel electrolytes.

Lithium thiophosphate glasses ionic conductivities, sample preparation methods, and properties have been investigated [8-11]. It has been reported that 0.95 Li$_3$PS$_4$ + 0.05 Li$_4$GeS$_4$, 0.75 Li$_2$S + 0.25 P$_2$S$_5$, 50 (0.67 Li$_2$S + 0.33
SiS$_2$) + 50 (0.75 Li$_2$S + 0.25 P$_2$S$_5$), 0.8 Li$_2$S + 0.2 P$_2$S has ionic conductivities on the order of $10^{-4}$ S/cm at room temperature [8-11]. Generally, Li$_2$S-PS$_{5/2}$ based glasses are prepared by melt quenches and mechanochemical synthesis [8-11]. They are often found as either glass-ceramics, ceramics, or glassy materials depending on the preparation process. Properties and sample preparation in the lithium sulfide binary vary differently than lithium thiophosphate. 0.5 Li$_2$S + 0.5 SiS$_2$ has a room temperature ionic conductivity on the order $10^{-4}$ S/cm [12]. These glasses can be prepared via rapid quenching of a high temperature melt or mechanical milling [13]. Mechanical milling utilizes high kinetic energies balls which impact a sample powder such as LiSiPS in order to form a glass.

This thesis focuses on similar lithium-based materials known as lithium thiosilicophosphate, more specifically along the compositional series 0.6Li$_2$S + 0.4[SiS$_2$+1.5(1-x)PS$_{5/2}$] (LiSiPS) for the development of high ionic conductivity glasses. The electrolyte series 0.6Li$_2$S + 0.4[xSiS$_2$+1.5(1-x)PS$_{5/2}$] was studied at 0.1 increments, and because of the rich lithium modifier mol fraction of 0.6, it is likely to permit high ionic conductivity. Combining both SiS$_2$ and PS$_{5/2}$ may provide positive synergistic properties and further promotes investigation into both glass formers.

The purpose of this research project was to prepare and study mixtures of the lithium thiosilicate and lithium thiophosphate to create lithium thiosilicophosphate glasses at various glass former mol fraction ratios, and to characterize their atomic level structure and thermal properties such as Tg and Tc. By finding thermal and atomic level properties, improvements in novel
battery electrolytes like good ionic conduction, thermal, and chemical stability, may one day be made.

The structures of LiSiPS are reported in this thesis. Compounds were prepared via mechanochemical synthesis. Infrared (IR) and Raman spectroscopy, X-Ray Diffraction (XRD), Differential Scanning Calorimetry (DSC), and Nuclear Magnetic Resonance (NMR) were utilized for chemical-physical characterization.
CHAPTER 2 BACKGROUND

2.1 All Solid State Electrolyte

A basic solid state battery is composed of a solid state electrolyte placed in between an anode and cathode, and each electrode is surrounded by a current collector as shown in Fig. 1. The anode and cathode electrodes are where the redox reactions for lithium transfer take place, while the solid state electrolyte-separator provides a physical barrier between both electrolytes and acts as a ion conducting medium [1, 14]. Solid state electrolytes are different than typical commercial liquid electrolyte batteries by having a solid barrier between the anode and cathode.

2.2 Review Of A Lithium Ion Conducting Battery

Lithium ion batteries are widely used in commercial cell phone, computers, tablets, and increasing electric vehicles. The advantageous technology comes from the lightweight of lithium metal with a density of 0.59 g.cm\(^{-1}\) permitting applications in portable electronics, its low reduction
potential of -3.04 V, and high theoretical specific capacity of 3860 mAh/g [15-17]. Lithium metal is also relatively abundant at about 0.0018 % of the earth’s crust making it economically feasible to implement lithium technology to a mainstream portable electronic market [18]. Even with all these advantages of lithium ion batteries, there are drawbacks.

For one, the full capabilities of lithium technology are not yet fully utilized. Commercial batteries use a LiMO₅ with specific capacities much lower than lithium metal, 274 mAhg⁻¹ (LiCoO₂) versus 3860 mAhg⁻¹ (Li metal), over a tenfold increase in capacity [17, 19]! If lithium metal anodes are used instead, more energy can be supplied to a load. However, it has been shown lithium metal anodes are highly prone to dendrite formation when used in liquid electrolyte lithium ion batteries [1, 2]. Preventing dendrite shorting is key for developing new all solid state batteries. In terms of using a lithium metal anode in a solid state battery, being one of the smallest elements in terms of radius will result in very high ionic conductivity through a solid glass electrolyte. High ionic conductivity also means that there is less voltage necessary to drive a current through the battery minimizing undesired heating and reaction, and making lithium metal anode batteries a very attractive energy storage candidate.

2.3 Dendrite Formation And Abuse Conditions

In transitioning from a liquid to solid state battery, it should ideally be more abuse resistant than conventional batteries and especially in regards to metallic lithium dendrite formation. Commercial batteries have a cathode material in form of a LiMO₅ such as lithium cobalt oxide LiCoO₂, lithium
manganese oxide LiMn$_2$O$_4$, and lithium iron phosphate LiFePO$_4$ [20, 21]. Although uncommon, LiCoO$_2$ dendrites can still form dendrites under extreme abuse conditions. Reactions 1-3 show intercalation/redox reactions in a LiCoO$_2$ battery, and provide insights into dendrite formation [22]:

Cathode: LiCoO$_2$ $\rightarrow$ $x$ Li$^{+}$ + $x$ e$^{-}$ + Li$_{1-x}$CoO$_2$ (1)

Anode: $x$ Li$^{+}$ + $x$ e$^{-}$ + 6 C $\rightarrow$ Li$_x$C$_6$ (2)

Cell Reaction: LiCoO$_2$ + 6C $\rightarrow$ Li$_{1-x}$CoO$_2$ + Li$_x$C$_6$ (3)

Under abuse conditions as lithium is cycled between electrodes, lithium metal can form and accumulate on the surface of an electrode extending out as moss-like, granular/particulate, or a needle-like dendrite [22-25]. If the dendrite extends out to the opposite electrode, the current shorts out causing free electron charge to transfer between LiMO$_x$ and Li$_x$C$_6$, causing the battery to heat up. Once a critical temperature is met an irreversible process known as thermal runaway takes place in which the battery becomes so hot that the liquid electrolyte decomposes, builds up pressure, and at worst case explodes causing a fire [26]. Under abuse conditions, conventional Li-ion batteries can experience detrimental effects due to external forces such as high temperatures and cold weather, and solid state batteries should overcome these drawbacks.

Thermal abuse tests involve taking batteries to extreme conditions to observe their failure point. In developing solid state electrolytes, they need to be stable in a wide range of temperatures. In one paper reported by Boon-Brett[27], thermal tests include raising lithium ion battery temperatures at 5 $^\circ$C steps for 30 minute holds until a final temperature of 200 $^\circ$C is reached, to observe the temperature at which thermal runaway occurs. Fortunately, in
using a solid state electrolyte, it is less likely that temperatures like 200 °C will trigger thermal runaway due to a physical barrier between both electrodes. The lithium dendrite is unable to penetrate the electrolyte and short, and so making it more likely to pass thermal abuse tests. Safer, and electrochemically stable batteries, and new solid electrolytes technology provide better solutions in thermal runaway suppression than conventional lithium ion conducting batteries.

Another abuse test evaluates the life of internal components of a battery due to low temperatures. An extreme cold test is designed to expose a lithium ion battery to sub-zero temperatures to replicate a sitting battery on a cold day. When batteries become extremely cold, the anode can exhibit a very high over potential while the ionic conductivity of lithium becomes poor, and this leads to the formation of dendrites, a precursor to thermal runaway [27, 28]. With the use of new solid electrolytes dendrite shorting can be prevented even in extreme cold temperatures, passing sub-zero temperature tests, and making all solid state batteries attractive alternatives to commercial lithium ion batteries.

To emphasize again the dangers of lithium ion batteries, fires were reported by the media in 2013 when an Boeing 787 Dreamliner aircraft battery overheated starting a fire and in 2014 when a Tesla Model S battery started a fire from overcharging [26, 29]. Battery hazards can be fatal, so research into innovative batteries materials, which are chemically stable, abuse resistant, and resistant to fire hazards, are critical.
2.4 Solid State Electrolytes

All solid state batteries may be able to solve some of the drawbacks associated with lithium ion batteries. A solid state battery uses a solid electrolyte to create a physical barrier between the anode and cathode. This in turn can make batteries more resistant to thermal runaway and safer [2] . Since solid state electrolytes can resist shorting of dendrites between the anode and cathode, lithium metal electrodes are now a viable optional material giving rise to batteries with high theoretical specific capacity of Li Metal [17] . There are a variety of methods for developing solid electrolytes for batteries since there are so many mixtures of glass formers and modifiers to consider. Electrolytes can be composed of glass formers like boron, silicon, germanium, aluminum, and antimony sulfide, when reacted with a network modifier like lithium sulfide [30-33]. These complex mixtures requires systematic approaches in identifying structures for optimal mixed glass former materials.

2.5 Glass Structure

Glassy materials are unique in nature since they are solids but retain the structure of a frozen liquid. Upon fast cooling, short-ranged order (SRO) and intermediate-ranged order (IRO) structures typically remain intact, but the long-ranged order (LRO) is usually not present since there is insufficient time to develop crystalline structures [34]. IRO structures are classified as a second nearest neighbor atom while SRO is the first neighbor. The lack of LRO indicates that the melt cooled quick enough to prevent crystal formation. Surprisingly, a material can also have only SRO and IRO, and still not be a
glass. These materials are called amorphous solids [35]. In order for a substance to be glass, it must exhibit a $T_g$; the onset glass transition region is called $T_g$. Upon heating a glass from below its $T_g$, energy will be absorbed into the glass giving SRO and IRO sufficient thermal energy to access viscoelastic diffusive motions and with further heating full viscosity motions will create the liquid state. $T_g$ is represented by a change in heat capacity, which is indicated by a thermal measurement through instruments like DSC. Glass formers studied in LiSiPS include SiS$_2$ and PS$_{5/2}$ to find variations in properties while changing their concentrations. Above the $T_g$ of the glass, but below the equilibrium melting point of the composition, the liquid is in a meta-stable state and is susceptible to free-energy driven crystallization. Crystallization results in a sharp exothermic peak.

2.5 Silicon Sulfide And Phosphorus Sulfide SRO Structures

The compositional series of glass formers and network modifiers studied in this thesis is 0.6Li$_2$S + 0.4[xSiS$_2$+1.5(1-x)PS$_{5/2}$]. Literature on Raman spectroscopy for lithium thiosilicate and lithium thiophosphate demonstrate special unit structures such as P$_0$, P$_1$, P$_{1P}$, Si$_0$, and E$^1$Si$_2$ [3, 36, 37]. To define each notation, the central atoms indicates either a silicon or phosphorus unit with an Si or P, and the superscript dictates how many linking sulfur extend to other localized structures in the glass network. These special notations for phosphorus and silicon units are shown in Fig. 2 and 3. P$_0$ and Si$_0$ units are isolated tetrahedral; P$_1$,P$_{1P}$ are dimeric groups; and E$^1$Si$_2$ are edge sharing units. Raman spectra reported for 0.7 Li$_2$S + 0.3 P$_2$S$_5$ glasses shows high population P$_0$ ortho-thiophosphate PS$_4^{3-}$, P$_1$ pyro-thiophosphate
P$_2$S$_7^{4-}$, and P$^{1P}$ ethane-like P-P bonds P$_2$S$_6^{4-}$ units giving rise to Raman emission bands at 425 cm$^{-1}$, 410 cm$^{-1}$, and 390 cm$^{-1}$ respectively, and are expected for the system studied in this thesis; 0.6 Li$_2$S + 0.4 [xSiS$_2$+1.5(1-x) PS$_{5/2}$] [3, 38]. Nuclear Magnetic Resonance (NMR) reported in literature agree with Raman assignments located at 83 ppm P$^0$, 90 ppm P$^1$, and 105 ppm P$^{1P}$ [32, 39]. The agreements between the Raman and NMR spectra helps confirm the structures Li$_2$S-P$_2$S$_5$ glasses. The secondary glass former investigated is silicon sulfide (SiS$_2$) and the Si SRO structural units were determined with Raman literature and through charge compensation [36, 40, 41]. Silicon SRO units were reported by Watson [36] in the yNa$_2$S + (1-y)SiS$_2$ (y = 0.33 to 0.7) system, and was compared to respective Li$_2$S-SiS$_2$ atomic structures [36]. E$^1$Si$^2$, Si$^4$, and Si$^0$ are shown at 373 cm$^{-1}$, 385 cm$^{-1}$, and 406 cm$^{-1}$ [36, 37, 41, 42]. It was expected that 0.6 Li$_2$ + 0.4 [xSiS$_2$+1.5(1-x)PS$_{5/2}$] will have similar Si units. Determining individual structural units in a glass can bring insights into properties in a glass like ionic conductivity, thermal, and chemical stability.
Figure 2: SRO Structural Si\textsuperscript{n} units expected in Li\textsubscript{2}S + SiS\textsubscript{2} glasses.
2.6 Mixed Glass Former Effect

The Mixed Glass Former Effect (MGFE) is described to be a non-linear, non-additive change in property with a constant modifier mole fraction and glass former concentration [43]. By keeping the modifier constant such as at 0.6 Li$_2$S and changing the glass former ratios, a trend in properties can be discovered. Changes in properties can be further quantified, and perhaps mathematical
predictions in characteristics can be made for analogous glass systems. In addition, structures based of SRO units can be related to thermal and electrical properties thereby helping determine the SRO with the best properties for a electrolyte in a battery. Once more is discovered about glassy electrolyte-separators through phenomena’s like the MGFE, developments into safe, thermally, and chemically stable batteries are more possible. Various systems were studied to determine how properties with a constant modifier and dynamic glass formers changes properties. A few MGFE systems investigated in literature include $0.3 \text{Li}_2\text{S} - 0.7 [(1-x) \text{SiS}_2 - x \text{GeS}_2]$, $0.33 \text{Li}_2\text{O} + 0.67 [x \text{B}_2\text{O}_3 + (1-x) \text{P}_2\text{O}_5]$, $0.35 \text{Na}_2\text{O} + 0.65 [x\text{B}_2\text{O}_3 + (1-x) \text{P}_2\text{O}_5]$ [43-46]. A closer look at $0.3 \text{Li}_2\text{S} - 0.7 [(1-x) \text{SiS}_2 - x \text{GeS}_2]$ shows variations in ionic conductivity from $x = 0$ to $x = 1$ which are mathematically very difficult to determine and in such case experimental measurements of the MGFE becomes necessary for conclusive evidence on properties in a mixed glass former system [44]. More MGFE experiments needs to be studied to gain insights into better mixed glass former electrolytes. Discovering the properties in MGFE system may one day reinvent solid state electrolyte technology making batteries more safe, fast ion conducting, abuse tolerant, and thermally stable. The MGFE studied in the thesis was LiSiPS.

2.7 Electrolyte Materials

Lithium thiosilicophosphate materials have been studied as separators extensively [39, 47-50]. The binary, lithium thiophosphate system was studied as a glass, ceramic, and glassy ceramic, and has relatively high ionic conductivity in the range of $10^{-4}$ to $10^{-3}$ S/cm at room temperature [38, 49, 50]. $0.67 \text{Li}_2\text{S} + 0.33 \text{P}_2\text{S}_5$, $0.67 \text{Li}_2\text{S} + 0.30 \text{P}_2\text{S}_5 + 0.03 \text{B}_2\text{S}_3$, $0.7\text{Li}_2\text{S} + 0.3 \text{P}_2\text{S}_5$,
have conductivities of 0.083, 0.141, and 4.2 mS/cm at room temperature making investigations for solid state electrolytes promising [49, 50]. P₂S₅ has also known to stabilize glassy materials against a lithium metal anode promoting stable redox reaction at the electrolyte-electrode interface [39, 47]. When 8% P₂S₅ was included in a 0.6 Li₂S + 0.32 SiS₂ + 0.08 P₂S₅ glass, cell resistance remained linearly constant during a cycle, with no erratic changes, meaning the electrolyte-anode stability improved with P₂S₅ [39, 47]. Takada reported similar behavior with good chemical reversibility in atomic structures with Raman spectroscopy by adding P₂S₅ as 0.38 Li₂S + 0.18 P₂S₅ and 0.44 LiI, showing that the addition of P₂S₅ can offer stability as an electrolyte when cycled [47]. Like P₂S₅ showing promise in chemical stability in cycling, SiS₂ also offer value in a mixed glass former system.

Li₂S-SiS₂ is also a good candidate for batteries. The binary compound 0.6Li₂S + 0.4SiS₂ has high conductivity of 0.5 mS/cm at room temperature showing promise in a mixed glass former electrolyte for improving conductivity properties [33]. Other electrolyte ternary materials include 0.63Li₂S + 0.36 SiS₂ + 0.01 Li₃PO₄, 0.36 Li₂S + 0.24 SiS₂ + 0.4 LiI with high ionic conductivities of 1.8 and 1.6 mS/cm [51]. A disadvantage to thiosilicates is their lack of chemical stability with the anode as compared to P₂S₅ during cycling. Raman spectra shows atomic unit structures varying in intensity before and after cycling the electrolyte 0.63 Li₂S + 0.36 SiS₂ + 0.01 Li₃PO₄, suggesting silicon sulfide is a less stable battery material [47]. Indeed, there may be problems in silicon’s stability, however it still serves as a potential separator candidate for solid electrolytes and combining with thiophosphate groups may in fact have synergistic effects.
2.8 Thermal Characteristic

Combinations of Li$_2$S-SiS$_2$ and Li$_2$S-PS$_{5/2}$ are attractive electrolytes from their relatively high Tg and Tc. Kennedy and Zhang [48] reported thermal properties on the composition 0.6 Li$_2$S + 0.4 [(1-x)SiS$_2$ + xP$_2$S$_5$] from x=0 to x=1 [48]. They showed an initial glass transition temperature (Tg) of 0.6 Li$_2$S + 0.4 P$_2$S$_5$ (x=1) at 208 °C monotonically increasing to 337 °C at 0.6 Li$_2$S + 0.4 SiS$_2$ (x=0), at increasing steps from x=0 to x=1 [48]. The crystallization temperature showed a similar trend, exhibiting exothermic peaks at ~288°C for 0.6 Li$_2$S + 0.4 P$_2$S$_5$ and almost linearly increasing toward 410 °C at 0.6 Li$_2$S + 0.4 SiS$_2$. This comes to show that increasing silicon sulfide content will increase the Tg and Tc, and with higher Tg’s and Tc’s internal battery chemical breakdown becomes less likely, thereby improving battery stability. Pradel [52] reported related behavior by varying modifier for xLi$_2$S + (1-x)SiS$_2$ and he showed that the Tg is barely affected with modifier concentrations between x=0.3 to x=0.6, only varying between 342 to 334 °C for the series. This shows that phosphorus sulfide plays a larger role in modifying thermal properties like Tg, Tc, and the glass working range than a binary Li$_2$S-SiS$_2$ system alone. In LiSiPS glasses explored in this thesis, it is expected that similar trends of Tg and Tc will arise with increasing SiS$_2$ content.

2.9 Mechanochemical Synthesis

Glasses can be synthesized with numerous techniques including an open crucible melt quench, sealed quartz ampoule melts, liquid nitrogen/ice rapid quenching, twin roller quenching, pulse laser vapor deposition, and mechanochemical synthesis [36, 48, 52-54]. Initial trials of open crucible melt quenching LiSiPS were between 600 to 800 °C and resulted in large mass
losses excess of 10% due to the low boiling point of PS$_{5/2}$ which is 540 °C at 1 atm, and high vapor pressure of 0.001 atm at 300 °C [55]. To overcome vaporization of PS$_{5/2}$, one can fill glassy materials in carbon coated sealed silica test tubes, and quenched the glasses rapidly, however these experiments are very costly, have a high risk of explosion due to the high vapor pressure of PS$_{5/2}$, and high risk of oxygen contamination from an intricate sealing process.

Another method pursued for reacting LiSiPS was use of the high energy balling milling technique called mechanochemical synthesis. Planetary milling uses a high strength mill pot and mill balls filled with sample powder. It relies on fast rotational velocities of mill balls to impact a sample powder converting kinetic energy from mill balls to chemical energy and form an amorphous glass [13, 56, 57]. An advantage of planetary milling LiSiPS is very low mass loss while still obtaining a glassy powder material, however the tradeoff is a glass with grain boundaries facilitating pathways for dendrites to grow. In addition, abuse resistance from thermal shock will likely be reduced since the thermal expansion of each grain will slightly vary creating points of cracks, wear, and fracture. Nonetheless, mechanochemical synthesis is a viable option for preparing the series LiSiPS. There may be concern if a glass can form from sample powders however it has been reported that ball milling 0.75Li$_2$S + 0.25 P$_2$S$_5$ and 0.6Li$_2$S + 0.4SiS$_2$ from 0 to 20 hrs at 370 rpm showed that glass formability improves with increased milling time [13, 58]. Common mechanochemical synthesis recipes are in the range of a 20 hour mill time at 350 rpm, with a 10 to 1 mass of balls (10 mm diameter) to sample powder ratio [8, 13, 58].
CHAPTER 3 OBJECTIVES OF THE THESIS

Mixed glass former glass solid electrolytes can be prepared by mixing a network modifier like Li$_2$S, and two glass formers such as SiS$_2$ and PS$_{5/2}$. This thesis focuses on LiSiPS electrolytes for developing conclusions about the MGFE. Li$_2$S, SiS$_2$, PS$_{5/2}$ all offer advantages such as the fast ionic conduction of Li$^+$ cations and the relatively low cost of SiS$_2$ and PS$_{5/2}$ allowing industry scale up for solid state electrolyte glass production.

Sulfide glasses inherently offer higher ionic conductivity due to the high polarizability compared to that of oxide-based glasses. The higher polarizability allows cations like Li$^+$ to be weakly bound to the sulfur anion, lowering the coulombic energy barrier, and thereby allowing facile hops between two SRO units. Another reason to pursue LiSiPS deals with the low cost of high purity PS$_{5/2}$ and SiS$_2$ glass formers. PS$_{5/2}$ offers properties in chemical and electrical stability shown through CV cycling [39, 47]. Silicon sulfide is also attractive because of good glass formability when quenched from high temperatures, and it is also a relatively low-cost material. SiS$_2$ and PS$_{5/2}$ may act synergistically when studying the series LiSiPS potentially offering insights into making batteries safer, and chemically, electrically, and thermally stable. In the present work, the atomic level structures of LiSiPS were explored as 0.6Li$_2$S + 0.4[xSiS$_2$ +1.5(1-x)PS$_{5/2}$] and their glass structures and thermal properties were explored to examine the correlations between their material properties and the SRO units structures that are comprised in the glass.

In LiSiPS, x was taken at 0.1 increments varying between the two glass formers PS$_{5/2}$ and SiS$_2$ in the series 0.6 Li$_2$S + 0.4[xSiS$_2$+1.5(1-x)PS$_{5/2}$]. Ideally, the Li$_2$S mole fraction is kept at a constant modifier to observe the MGFE,
however issues arose in crystallization at a high modifier contents in the series 0.65Li$_2$S + 0.35[xSiS$_2$+(1-x)PS$_{5/2}$] and the series 0.6 Li$_2$S + 0.4 [xSiS$_2$+1.5(1-x)PS$_{5/2}$] was pursued instead to obtain glass electrolytes. The ternary diagram in Fig. 4 shows specific glasses studied at 0.65 Li$_2$S and 0.6 Li$_2$S modifier. The compositional line for 0.6Li$_2$S + 0.4[xSiS$_2$+1.5(1-x)PS$_{5/2}$] is in black, while the composition line for 0.65Li$_2$S + 0.35[xSiS$_2$+(1-x)PS$_{5/2}$] is in red in Fig. 4. The red line at 0.65Li$_2$S modifier remains constant and flat across the entire series. The 0.6Li$_2$S modifier is in black, is angled down to 0.5Li$_2$S, achieving the binaries 0.5Li$_2$S + 0.5 PS$_{5/2}$ and 0.6Li$_2$S + 0.4SiS$_2$ from x = 0 to x = 1. With the transition from 0.65Li$_2$S to 0.6Li$_2$S in LiSiPS a definitive glassy series was found, and investigations into the MGFE began.

Figure 4. Ternary diagram for Lithium thiosilicophosphate
CHAPTER 4 EXPERIMENTAL METHODS

4.1 Material Synthesis

4.1.1 SiS$_2$ Material Preparation

Silicon sulfide was prepared via a quartz silica reaction ampoule. The ampoule was evacuated for 15 minutes through a liquid nitrogen cold trap under rough pump vacuum so that the internal pressure was less than 50 mtorr. The evacuated ampoule was flame dried for 3 minutes to remove moisture inside the silica glass. During this flame treatment, water adhered to the surface of the glass will vaporize preventing water contamination into raw material. Dimensions of the tube were 36 mm ID X 40 mm OD with a 152 mm length. Elemental crystalline silicon powder (99.999%, Alfa Aesar) and elemental sulfur chunks (99.999%, Acros Organics) were weighed out in appropriate amounts to ±0.0005 grams and then premixed in a Spex Mill 8000 mixer for 1 minute. Batch weights varied between 28 to 40 grams. The SiS$_2$ reaction takes place over two days with a final temperature of 924°C as shown in Fig. 5 and is cooled down over several hours by simply letting heat dissipate from the furnace.

![Figure 5. Heating profile for SiS$_2$ synthesis](image-url)
Once the ampoule and the reacted SiS$_2$ was cooled back to room temperature, the SiS$_2$ filled ampoule was brought inside the N$_2$ glove box and handled in an inert N$_2$ atmosphere. Good SiS$_2$ is white and gray in color. It can be either powdery or in chunks. The chunks were Spex milled once again to obtain a powdery substance. The final product has similar Raman and IR spectra to literature data [37, 59].

4.1.2 Lithium Thiosilicophosphate Glasses

All samples were prepared in an inert N$_2$ atmospheres to prevent water or oxygen contamination. Four gram batch sizes of appropriate amounts of Li$_2$S (99.9%, Alfa Aesar), PS$_{5/2}$ (98+%, Acros Organics), and SiS$_2$ (Lab synthesized, see above) were massed out in stoichiometric amounts and poured into a zirconia planetary mill pot. A rubber O-ring is on the top lip to ensure an airtight seal. The packed mill pot was placed on a counter weight, and to prevent leakage, the zirconia lid was clamped down onto the pot with an aluminum plate. Fig. 5 shows a mixture of 0.6Li$_2$S + 0.4 [xSiS$_2$ + 1.5(1-x)PS$_{5/2}$] at x = 1, mechanically milled for 1 hour at 450 rpm. Each zirconia ball is coated with a white powder of LiSiPS and is caked around the yellow walls of the ZrO$_2$ container.
The ratio of zirconia balls to raw material powder was 12 to 1 with an average ball diameter of 10 mm. As compared to literature, the ratio is greater than 10 to 1 permitting good mechanochemical synthesis since there is more available mass to strike the powdered material [8, 13, 58]. The sample was rotated at 450 RPM for 20 hours with a reversed rotation every 30 minutes. The impact of the zirconia balls with the powder reacts Li₂S, SiS₂, PS₅/2 into an amorphous structure. Post reaction, the zirconia mill pot is taken from the planetary mill and evacuated for 20 minutes and placed inside the glovebox. Upon opening the mill pot, free sample powder remains at the base, however much of the samples is adhered to the walls of the zirconia mill pot and to the surfaces of the milling media. A chisel and hammer are used to scrape the material until it is removed. On a good removal, about 88% of a 4 gram batch can be removed. This is sufficient to perform other structural & thermal analysis.
techniques. As $x$ increases from $0.6\text{Li}_2\text{S} + 0.4[\text{xSiS}_2+1.5(1-x)\text{PS}_5\text{S}_2]$, the reacted powder changes from a white to mustard color.

4.2 Instrumentation

4.2.1 Fourier Transform Infrared Spectroscopy

A Bruker IFS 66v/s, Fourier transformed infrared spectrometer (FTIR) was utilized to characterize planetary milled glasses. Far IR and Mid IR ranging from 120 to 4,000 cm$^{-1}$ was the targeted scanning range. Two beam splitters, KBr and Opus T222, were used to collect the full IR spectra, there were manually switched from Mid to Far IR. CsI and glass powder were mixed in a ratio of about 200:3 with a mortar & pestle, and then pressed at 1.75 tons for 2 minutes in a Specac Mini-Pellet Press 2T. Each die contained approximately 3mg of glass and 200mg of CsI. Far IR and Mid IR resolution was 4 cm$^{-1}$ with a total of 32 scans. All compounds used in these experiments required very dry atmospheric conditions. The pressed die were removed from the glovebox in a sealed vial and placed in a specially modified transparent IR case which covered the sample holder, a space large enough to attach a rubber glove in the spectrometer. Nitrogen gas flowed into the sealed container permitting highly inert atmospheric conditions for IR testing.

4.2.2 Raman Spectroscopy

A Renishaw inVia Raman microscope was used to collect the Raman spectra of the synthesized materials. A confocal microscope using 20X and 50X magnification objectives allowed accurate focusing on a sample’s surface. Collecting good data over scattered uneven powders can be difficult due to
inconsistent surface morphology, therefore each sample was pressed in an MTI 15 T Laboratory Press to obtain flat, circular pellets. A plastic sample holder with a quartz slide was vacuum sealed containing the pressed sulfide-based pellet. A Raman 20 mW 488 nm Argon laser scanned over a pressed pellet at 100% power permitting good S/N ratios for analysis. A general survey scan was completed to make sure there was correct focusing. A static scan allowed maximum signal for a specific range, 100 cm\(^{-1}\) to 873 cm\(^{-1}\).

4.2.3 Differential Scanning Calorimetry

Thermal measurements of the T\(_g\) and crystallization temperatures (T\(_c\)) were measured. Aluminum pans were packed with about 10 mg of powder and cold welded with a press. Each sample was surveyed to obtain T\(_g\), T\(_c\), and a \(\Delta T\) (T\(_c\)-T\(_g\)). The samples were scanned in a Pyris Diamond DSC that was heated at 20\(^\circ\)C/min to 400 \(^\circ\)C for a survey scan and was later cycled above the onset glass transition temperature. The highest temperatures measured were up to 400 \(^\circ\)C to prevent unwanted gaseous sulfur from reacting with the aluminum pans thereby protecting the instrument.

4.2.4 X-Ray Diffraction

The amorphous nature of LiSiPS samples were determined through XRD. A Rigaku Smart Lab X-ray Diffractometer was used to scan the samples at 0.01 steps, under a continuous scan mode setting. Each sample was grounded down to a fine power with a mortar and pestle. An x-ray transparent sample holder with an o-ring type seal was used to transfer the sample between the glovebox and the XRD. The sample was poured into a zero-background
silicon plate, flattened with a spatula, and scanned from 25 theta to 90 \( \theta \). The silicon plate reduced the necessary mass from about 2 grams to 0.5 grams, however the cost was a limited scan range from 20 to 120 \( \theta \).

4.2.5 Nuclear Magnetic Resonance

Magic angle spinning Solid-State NMR is a special analytical technique to directly target specific nuclei interactions for SRO analysis. A 4 mm zirconia rotor, rubber funnel, and packing tool was used to prepare each sample. The rotor was inserted into a 600 MHz Advance II Bruker instrument and was spun at 12,000 Hz. Higher spinning speeds up to 14,000 Hz are attainable making spinning side bands more apparent, however out of safety of the instrument, 12000 Hz was chosen throughout LiSiPS. The 31P \( t_1 \) relaxation time was 300 seconds, pulse length of 3 \( \mu \)s, with a sum of 96 scans, and adding up to 6 hours per experiment. The relatively short relaxation times of 31 P, and a high abundance of NMR spin \( \frac{1}{2} \) active nuclei of 100%, permitted highly resolved results. Limited access to NMR prevented further analysis on 29 Si. Bruker Top Spin v3.5 and DM Fit 2015 were software analysis tools used for spectral analysis and deconvolution.
CHAPTER 5 RESULTS AND DISCUSSION

5.1 Structural Characterization

5.1.1 X-Ray Diffraction

Initial work in Li$_2$S-SiS$_2$-PS$_{5/2}$ glasses were completed at a relatively high mole fraction modifier, 0.65Li$_2$S + 0.35[xSiS$_2$+(1-x)PS$_{5/2}$] at 0.1 increments. The large amount of Li$_2$S resulted in rapid crystallization indicated by relatively sharp XRD peaks as shown in Fig. 7. Large, unincorporated Li$_2$S peaks can be shown at 27, 31, 45, 53, 56 2θ as a result of having too much modifier in the series [60]. The goal of the project was to obtain glasses, so to improve amorphous nature of 0.65 Li$_2$S + 0.35 [xSiS$_2$ + (1-x)PS$_{5/2}$], a lower modifier was chosen instead.

An alternative system studied with improved glass formability was 0.6Li$_2$S + 0.4[ xSiS$_2$ + 1.5(1-x)PS$_{5/2}$] at 0.1 increments as shown in Fig. 9. The overall nature of the spectra is amorphous. Small peaks corresponding to crystalline components containing Li$_2$S and elemental Si can be seen at x = 0.5, 0.8, 0.9, and 1. Li$_2$S peaks may be attributed small amounts of excess Li$_2$S being unincorporated to the glass structure. Elemental silicon is found at 28, 47, and 56 2θ and comes about from Si ejection during high energy ball milling SiS$_2$[56]. The overall low intensity broad-spectrum confirm an overall amorphous nature in the LiSiPS series. In these next sections, the IR and Raman spectra will be discussed to confirm the structural units, contamination, and elements like Si present in the glasses.
Figure 7: Li$_2$S peaks in 0.65 Li$_2$S + 0.35[xSiS$_2$+(1-x)PS$_{5/2}$]
Figure 8: Amorphous nature in $0.6 \text{Li}_2\text{S} + 0.4[\text{xSiS}_2+1.5(1-x)\text{PS}_2]$
5.1.2 Infrared Spectroscopy

LiSiPS vibrational modes were analyzed with FTIR, covering the mid-IR and far-IR, 4000 to 150 cm$^{-1}$. An amorphous nature of Si and P units are present for all materials as shown in Fig. 10. The presented data ranged between 200 and 1000 cm$^{-1}$; since this is where there is most IR activity of the Li-S, Si-S, and P-S stretches as well as where oxygen contamination occurs. The basic building blocks for 0.6Li$_2$S + 0.4 [xSiS$_2$+1.5(1-x)PS$_{5/2}$] are composed of SRO structures displayed from x=0 to x=1. Expected compounds are orthothiophosphate PS$_4^{3-}$, pyrothiophosphate P$_2$S$_7^{4-}$, and P$_2$S$_6^{4-}$ ethane like P-P structures [3, 38, 61]. Considering high concentration phosphorus groups in the compositional range from x = 0 to x = 0.4, the IR spectra shows that the Li$_2$S-PS$_{5/2}$ structure is composed of dimeric P-S stretches associate with P$^1$ and P$^{1P}$, and isolated tetrahedral P$^0$ networks. Four large peaks are presented at 328 cm$^{-1}$, 475 cm$^{-1}$, 587 cm$^{-1}$, and 607 cm$^{-1}$. An intense broad band extends between 150 to 430 cm$^{-1}$ and is attributed to Li-S vibrations [62, 63]. The IR modes at higher wavenumbers arise from P-S stretches at 607 cm$^{-1}$ and 475 cm$^{-1}$, which are both attributed to the P$^1$ SRO [61].

Between 0 ≤ x < 0.3, a mode attributed to the P$^{1P}$ SRO unit is at 587 cm$^{-1}$ and appears as one of the more intense peaks in the IR spectra of the LiSiPS glasses and this trend in intensity of P$^{1P}$ continues to x = 0.9, where in fact the addition of SiS$_2$ does not change the peak intensity as rapidly as compare to P$^1$. Between the 0 ≤ x < 0.3 range is P$^1$, and it is initially large at 607 cm$^{-1}$, however once x ≥ 0.3, it drops subtly in intensity parallel to the asymmetric stretching P$^1$ at 475 cm$^{-1}$, and by x = 0.6 can no longer be seen. P$^0$ units are located in the 543 cm$^{-1}$ region, which are strongly overlapped by other P and Si units. Very
low intensity oxygen contamination from either P-O or S-O exist between 850 to 1200 cm\textsuperscript{-1} confirming good purity of LiSiPS\cite{51, 64, 65}.

More towards the thiosilicate end, Si-S vibrations can be seen around 468 cm\textsuperscript{-1} and 566 cm\textsuperscript{-1}, and a small peak at 933 cm\textsuperscript{-1} \cite{33, 36, 51, 66}. At 468 cm\textsuperscript{-1}, 0.1 ≤ x ≤ 0.5, there is an overlap between P-S and Si-S vibrational modes, however from 0.5≤x≤1 the overlap is less apparent revealing Si-S modes remaining in similar intensity on the high SiS\textsubscript{2} concentration portions of the series. At 566 cm\textsuperscript{-1}, from 0.1≤x≤1, Si-S modes remain at high intensities showing no large change in structure intensity, and indicating that one type of structure, for example Si\textsuperscript{0} remains with large intensity through the series. The Si-S stretch at 933 cm\textsuperscript{-1} slowly increases in intensity as more SiS\textsubscript{2} is added. Oxygen contamination remains minimal from 1000 to 1200 cm\textsuperscript{-1} attributed to S-O and Si-O stretches ensuring highly pure LiSiPS samples \cite{51, 65, 67}. In addition to IR, Raman demonstrates similar trends in SRO and will be discussed in the next section.

Figure 9: Infrared spectra of 0.6Li\textsubscript{2}S + 0.4 xSiS\textsubscript{2}+1.5(1-x)PS\textsubscript{5/2}
5.1.3 Raman Spectroscopy

Raman analysis was completed on the LiSiPS series at 0.1 increments as shown in Fig. 12. Due to the overlap of Si and P Raman modes sharing a similar spectral region between 380–425 cm$^{-1}$, deconvolution of overlapping peaks is necessary as shown in Fig. 13. The spectra reveal modes that are consistent with the Si and P SRO units that have been assigned in literature [3, 38, 61]. More specifically thiophosphate groups suggested are presented as P$^1$, P$^{1P}$, and P$^0$, and this is consistent with the collected Raman data. As $x$ increases from 0 to 1, phosphorus units transition from P$^1$ at 404 cm$^{-1}$ to P$^0$ at 420 cm$^{-1}$. In other words, at $x=0$ P units primarily link to other SRO structures with a single BS, however as SiS$_2$ increases in concentration, P units lose their ability to link by a BS and form P$^0$ units instead. P$^{1P}$ SRO shoulder units are also presented by a mode at 397 cm$^{-1}$ that slowly decreases in intensity with increasing SiS$_2$ content. Very low intensity polysulfide S-S stretching modes can be seen around 150, 220, and 479 cm$^{-1}$ as shown from $x = 0$ to $x = 0.4$. Theoretically at 0.6Li$_2$S + 0.6PS$_{5/2}$ ($x=0$) P$^1$ forms SRO units at 100% population, however experimentally it can be seen that relatively large amounts of P$^1$ as well as significant amounts P$^{1P}$ form. The presence of P$^{1P}$ may in fact come from P$^1$ losing a BS, forming small amounts of free polysulfides and P$^{1P}$ units. Similar structural tetrahedral behaviors in Li$_2$S-PS$_{5/2}$ tetrahedral units can be seen in the Li$_2$S-SiS$_2$ system.
Figure 10: Raman spectra of 0.6 Li$_2$S + 0.4 [x SiS$_2$ + 1.5 (1-x) PS$_{5/2}$]
Figure 11: Deconvoluted spectra of $0.6 \text{Li}_2\text{S} + 0.4 \left[ x \text{SiS}_2 + 1.5 (1-x) \text{PS}_{5/2} \right]$
As reported by Watson [36] who examined melt quenched glasses in the sodium analog yNa$_2$S + (1-y)SiS$_2$ (y = 0.33 to 0.7) series, a sharp center peak with two broad shoulders is shown in the LiSiPS glass series. From the thiosilicate binary, there are large peaks at 372 cm$^{-1}$, 385 cm$^{-1}$, and 410 cm$^{-1}$ formed from dimeric and tetrahedral groups [36]. Going into more detail the largest peak at 385 cm$^{-1}$ are Si$^0$ SRO groups and are observed as the main building block at x = 1, with two broad shoulders of E$^1$Si$^2$ (410 cm$^{-1}$) and Si$^4$ (372 cm$^{-1}$) supporting units. At x = 1, the fraction of the Si$^0$ SRO group are maximum. From 0.6≤x≤1, the fraction of Si$^0$ SRO groups maintains a steadily decreasing concentration. However, when x≤0.5, there is a quick decay in the fraction of the Si$^0$ SRO units. SiS$_2$ loses its ability to form edge sharing E$^1$Si$^2$ units with increasing PS$_{5/2}$, and at x=0.6 becomes undetectable in Raman. A relatively small Si$^4$ peak is present in the glasses from 0.2≤x≤ 1, and by x=0.2 reaches a minimum intensity. From 0.4≤x≤ 1, a very intense peak appears at 520 cm$^{-1}$, corresponding to elemental Si, which is surprising since no elemental silicon was found in lab-made silicon sulfide [68]. This means Si is being ejected during mechanochemical synthesis. To try to find the cause of Si ejection, more Raman experiments were completed.

One reason for ejection in mechanochemical synthesis of LiSiPS is that reactions are taking place at too high of an rpm, and for too long of time, causing excess energy input into LiSiPS resulting in Si ejection. Tatsumisago [13] reported a ball milling time of around 370 rpm for 20 hours to obtain a completely homogenous glass with no evidence of Si ejection shown from XRD. In short, less rpm equates to less energy into LiSiPS for glass formation, which may prevent the reaction for Si to eject. To test this hypothesis instead of ball
milling LiSiPS at 450 rpm for 20 hours, these parameters were reduced to 370 rpm at incremental times from 1 to 20 hrs. Fig. 13 shows 0.6Li$_2$S + 0.4SiS$_2$ ($x=0$), ball milled at 370 RPM at 1 hr, 5 hr, 10 hr, and 20 hr time intervals. At 1 hr the reaction is incomplete, however elemental Si is already ejected indicated by the 520 cm$^{-1}$ peak. Not only that, since Si is ejected, small amounts of Li$_2$S that should be associating with Si units, may actually become unincorporated ranging from $\sim$370-373 cm$^{-1}$ and overlapping with Si$^4$ structures [69]. As milling time increases, elemental Si saturates at 10 hours. Even at 370 rpm intense Si peaks are still present, so perhaps there is another phenomena causing silicon to eject independent of high rpm speeds.

Another hypothesis is that the Si develops from mechanically milling SiS$_2$ and is unrelated to network modifier Li$_2$S and glass formers SiS$_2$-PS$_{5/2}$. To test this, SiS$_2$ was mechanically milled at 450 rpm at 0, 5, 15, 25, and 35 hrs as shown in Fig. 14. By a 5 hour milling time the SiS$_2$ was completely amorphous and silicon ejection completely saturates showing that SiS$_2$ is prone to losing Si from high energy ball milling. All other times up to 35 hours are mirror images of each other, and so no further reaction takes place.

Looking more closely at the polysulfide region for Li$_2$S-SiS$_2$ glasses shown in Fig. 15, can present more detail on how much sulfur is being incorporated at the 0.6Li$_2$S + 0.6PS$_{5/2}$($x=0$) and 0.6Li$_2$S + 0.4SiS$_2$($x=1$). The most obvious S-S stretches should occur at 153 cm$^{-1}$ and 217 cm$^{-1}$, blended in with E and F$_2$ amorphous vibrational modes at 140 and 182 cm$^{-1}$, however there is little evidence to support polysulfide formation. Although there is little indication of polysulfides in Li$_2$S-SiS$_2$, there is still a chance of formation on the Li$_2$S-PS$_{5/2}$ end. The broad band in 0.6Li$_2$S + 0.6PS$_{5/2}$ shows peaks from
phosphorus sulfide as well as some small indication for polysulfide’s around 153 cm\(^{-1}\) and 217 cm\(^{-1}\). Based on Raman results, \(P^1\), \(P^{1p}\), \(P^0\), \(Si^1\), \(Si^0\), \(Si^4\), and elemental Si are formed by high energy ball milling \(0.6 \text{Li}_2\text{S} + 0.4[\text{SiS}_2 + 1.5(1-x)\text{PS}_{5/2}]\). A technique that further confirms the formation of SRO is NMR.

Figure 12: \(0.6 \text{Li}_2\text{S} + 0.4 \text{SiS}_2\) milled at 450 rpm to observe Si ejection
Figure 13: SiS$_2$ milled at incremental times for observation on Si ejection
Figure 14: Low wavenumber comparison on raw materials, SiS\textsubscript{2}, S, and PS\textsubscript{5/2}. 

0.6 Li\textsubscript{2}S + 0.6 PS\textsubscript{5/2} 

PS\textsubscript{5/2} 

S 

SiS\textsubscript{2} 

0.6 Li\textsubscript{2}S + 0.4 SiS\textsubscript{2} 

Raman Shift (cm\textsuperscript{-1})
5.1.4 Nuclear Magnetic Resonance

Specialized characterization techniques like NMR permits the examination of various SRO structures that are present in LiSiPS. $^{31}$P nuclei were examined to observe various SRO structure. After P units were determined through deconvoluted NMR spectra, approximate values of Si units concentrations were determined by charge compensation requirements. The $^{31}$P MAS NMR spectra showed that SRO groups were mainly composed of $P^{1P}$, $P^0$, and $P^1$ groups and these units are consistent with the IR and Raman spectra. $^{31}$P MAS NMR experimental spectra for glasses between $x=0$ to 1 at 0.1 increments are shown in Fig. 15. $P^1$ is located at 90 ppm, $P^{1P}$ at 105 ppm, and $P^0$ at 82 ppm. As $x$ increases from 0 to 1, the SRO order varies in peak intensity. The assignments made here agree with what those reported in literature [3, 32, 38, 39, 70]. Due to the overlapping nature of the peaks, the spectra were deconvoluted which are presented in Fig. 16. To better follow experimental SRO trends, a compositional map was made, Fig. 17. Here $P^1$ is very intense at $x=0$ making up about 85% of the phosphorus population, and $P^{1P}$ makes up 15%. $P^1$ exhibits a rapid change in intensity between $0 \leq x \leq 0.4$, where the $P^0$ unit becomes the majority at $x=0.4$ and $P^0$ is 41%, $P^1$ is 12%, and $P^{1P}$ is 6.5%. At the low mol fraction region $0 \leq x \leq 0.2$ $P^{1P}$ reaches a maximum value 17%, and steadily lowers in intensity parallel to $P^1$ as $x$ increases to 1. $P^0$ is the most populated phosphorus unit on high SiS$_2$ concentrations, at $x=0$, 9.7% are $P^0$, 0.26% are $P^{1P}$, and $P^1$ at 0%. This means as SiS$_2$ is incorporated into the glass network phosphorus units lose their ability to bond to other SRO structures transitioning from $P^1$ SRO units to $P^0$. In Fig. 17, associated Li$^+$ were charge compensated. $PS_{52}$ SRO are associated with Li$^+$ charges where theoretical
values and experimental values must add up stoichiometrically to develop conclusive evidence on presented units.

At the binary 0.6Li$_2$S + 0.6PS$_{5/2}$($x=0$) the modifier and glass former have a 1 to 1 ratio. This leaves 1 Li$_2$S to 1 PS$_{5/2}$, and combining these together is written as Li$_2$PS$_{7/2}$, also known as a P$^1$ unit referenced in Fig. 3. The P$^1$ has 2 NBS, that is with 2 associated Li$^+$ ions, connected each by single bonds to the central P atom, and one BS bonded shared between another SRO unit. Here the Li$^+$ cations are localized around NBS so for a P$^1$ unit there are two Li positive cation charges. A similar matchup can be shown for 0.6 Li$_2$S + 0.4 SiS$_2$($x=1$), with a ratio of 3 to 2, that is 3Li$_2$S + 2SiS$_2$, and added together create Li$_6$Si$_2$S$_{7/2}$ or Si$^1$. Each sulfur in Si$^1$ has 3 associated Li$^+$ localized around a NBS. Theoretically, the amount of Lithium charges must be conserved, with a -2 charge for each P$^1$ unit, and a -3 charge for each Si$^1$. Although no Si NMR experimental results were presented in LiSiPS, theoretical values are shown in Fig. 17, created through charge compensation units, and literature comparisons.

At 0.6Li$_2$S + 0.4SiS$_2$ there should be a theoretically -3 charge associate with Si$^1$, however literature reports experimental values as high as -3.5 for the Li$_2$S-SiS$_2$ binary. This large discrepancy required revised theoretically values for 0.6Li$_2$S + 0.4SiS$_2$ since the ratio between modifier and glass former in fact increases. To account for the extra charge Si$^0$, E$^1$Si$^2$, Si$^2$, and Si$^{1\text{Si}}$ were added as units. Comparison between experimental and revised theoretical charges can be shown in Table 1.
Table 1: Experimental and Theoretical Comparison of NBS

<table>
<thead>
<tr>
<th>X</th>
<th>Experimental P and Si</th>
<th>Theoretical</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-2.00</td>
<td>-2</td>
<td>0.00</td>
</tr>
<tr>
<td>0.1</td>
<td>-2.08</td>
<td>-2.15</td>
<td>-3.33</td>
</tr>
<tr>
<td>0.2</td>
<td>-2.29</td>
<td>-2.3</td>
<td>-0.51</td>
</tr>
<tr>
<td>0.3</td>
<td>-2.40</td>
<td>-2.45</td>
<td>-2.02</td>
</tr>
<tr>
<td>0.4</td>
<td>-2.61</td>
<td>-2.6</td>
<td>0.39</td>
</tr>
<tr>
<td>0.5</td>
<td>-2.70</td>
<td>-2.75</td>
<td>-1.76</td>
</tr>
<tr>
<td>0.6</td>
<td>-2.75</td>
<td>-2.9</td>
<td>-5.34</td>
</tr>
<tr>
<td>0.7</td>
<td>-2.84</td>
<td>-3.05</td>
<td>-6.82</td>
</tr>
<tr>
<td>0.8</td>
<td>-3.01</td>
<td>-3.2</td>
<td>-6.03</td>
</tr>
<tr>
<td>0.9</td>
<td>-3.20</td>
<td>-3.35</td>
<td>-4.43</td>
</tr>
<tr>
<td>1.0</td>
<td>-3.43</td>
<td>-3.5</td>
<td>-2.06</td>
</tr>
</tbody>
</table>

As shown in XRD and Raman, small amounts of Si are ejected resulting in the Li$_2$S and sulfur originally associated with edge-sharing SiS$_2$ units to transfer to other units that hold more charge like Si$^0$. The excess charge associated with Li$_2$S-SiS$_2$ as reported in literature have a -3.5 charge, comes from fact that a large number of Si$^0$ units form, 69% at x=1. These Si$^0$ units are isolated tetrahedral containing purely NBS holding -4 charge at each corner. Along at x=1 are Si$^2$ at 16%, ESi$^2$ 10%, and Si$^{1Si}$ at 5% accounting for a total charge of -3.43 at x = 1 comparatively close to theoretical -3.5 with only -2%
difference [41]. As x rises from 0 to 1 there is a rapid increase in Si\textsuperscript{0} units and steady increase in Si\textsuperscript{2}, ESi\textsuperscript{2}, and Si\textsuperscript{1[Si]} units. The larger discrepancies in percent difference between 5\(\leq\)x\(\leq\) 1 exceeding -5\% at x = 0.6, 0.7, and 0.8 have to deal with the theoretical Si units which do not accurately represent true experimental units presented in LiSiPS. These silicon units presented were taken from literature, and charge compensation with respect to 31 P, and therefore 29 Si NMR on LiSiPS experimental results are needed to officially confirm the presence of types of Si SRO units. Comparatively P units expected at x = 0 are P\textsuperscript{1} and P\textsuperscript{1P} and are charge compensated to have a total -2 at the Li\textsubscript{2}S-PS\textsubscript{5/2} binary with 0\% difference with respect to the theoretical value. In high PS\textsubscript{5/2} concentrations 0\(\leq\)x\(\leq\)5 theoretical and experimental charges can be accounted for with less than a 5 percent difference. At worse case x = 0.1, where charge varies by a -3.33\%. The good accuracy of theoretical and experimental results in 31P at high concentrations is due to good experimental preparation allowing highly resolved NMR results, and accurate deconvolution of experimental 31 P NMR data. Structural characterizations were discussed with the help of XRD, Raman, IR, and NMR techniques and the type of SRO revealed will have an effect on thermal properties.
Figure 15: Raw NMR spectra of $^{31}$P
Figure 16: NMR Spectra of $^{31}$P in LiPSiS
Figure 17: Population of phosphorus units
5.2 Thermal Characterization

Each sample was examined by DSC to observe thermal phenomena like Tg and Tc. From x=0 to x=1, the DSC scans for the LiSiPS glasses are shown in Fig. 19. Endothermic peaks that rise up refer to the onset Tg’s, and the large downward peaks refer to onset Tc’s. By visual inspection, from x = 0 to x = 1, there are large shifts in Tg/Tc from left to right indicating a rising Tg/Tc with increasing SiS\textsubscript{2} content. Kennedy and Zhang [48] reported similar Tg and Tc temperature transitions in 0.6Li\textsubscript{2}S + 0.4[xPS\textsubscript{5/2} + (1-x)SiS\textsubscript{2}], where the increase in SiS\textsubscript{2} increased the Tg and Tc, having an initial and final Tg of 208 and 337 °C, and initial and final Tc of 288 and 410 °C [48]. The series 0.6 Li\textsubscript{2}S + 0.4 [ x SiS\textsubscript{2} + 1.5(1-x)] behaves similarly by increasing in Tg and Tc with increasing SiS\textsubscript{2} content indicated more clearly by plotting Tg and Tc trends in Fig. 20. Based off these DSC results, the thermal window for Tg’s and Tc’s is between 226°C and 348 °C.

The binary silicon end 0.6 Li\textsubscript{2} + 0.4 SiS\textsubscript{2} (x=1) has a Tg/Tc of 312/348 °C while the phosphorus end 0.6 Li\textsubscript{2}S + 0.6 PS\textsubscript{5/2} (x=0) is observed at 226/264 °C. There is a non-linear increase trend in crystallization and glass transition temperatures with the addition of silicon sulfide. Pradel [52] showed that the Tg’s of x Li\textsubscript{2}S + (1-x) SiS\textsubscript{2} glasses are primarily dictated by glass formers and not modifier concentrations, that is between x = 0.3 to x = 0.6 Tg varies between 331 to 341 °C, only a 10 °C difference. For a binary series of Li\textsubscript{2}S and SiS\textsubscript{2} this may be the case, however with the addition of PS\textsubscript{5/2} the Tg’s/Tc’s of these values rise significantly, that is between 226 to 312 °C. At high PS\textsubscript{5/2} content 0\leq x\leq0.3, Tg varies little between 226 to 234 °C, an 8 °C difference, and Tc between 264 °C to 276 °C, only a 12 °C difference, meaning SiS\textsubscript{2} incorporation...
into Li$_2$S-PS$_{5/2}$ has little effect on the thermal sets at high PS$_{5/2}$ concentrations. From $0 \leq x \leq 1$, there is a steady increase in $T_g/T_c$, both maximizing at $x=1$. Ultimately, the non-linear and non-additive increase in $T_g$ and $T_c$ in LiSiPS refers to a negative MGFE at work.

Figure 18: DSC traces showing $T_g$ and $T_c$
Figure 19: Transition temperature comparison with mol fraction X
CHAPTER 6 CONCLUSIONS AND FUTURE WORK

Novel solid state electrolytes are of interest for developing next generation battery technology. New LiSiPS glasses were prepared through planetary milling $0.6\text{Li}_2\text{S} + 0.4[x\text{SiS}_2 + 1.5(1-x)\text{PS}_{5/2}]$ at 450 rpm for 20 hours, as a solid electrolyte. The goal of developing ternary solid state electrolytes was to study the MGFE and find good properties for electrolytes, which are thermally and chemically stable. For LiSiPS structural and thermal properties were characterized with techniques like XRD, Raman, IR, and NMR. XRD results showed a mostly amorphous system with minor peaks coming from unincorporated Li$_2$S and elemental Si. IR showed various Si-S, and P-S stretches with very low oxygen contamination. Raman revealed vibrational modes in P and Si structures. Specifically P units in LiSiPS varied from $P^1$ to $P^0$, with more silicon sulfide content, and silicon's most populated units were primarily Si$^0$. Determined through 31 P NMR, at $x=0$ SRO structures are $\sim$85% $P^1$ units and $\sim$15% $P^{1P}$, and by $x = 0.9$ $P^0$ makes up 9.7% while $P^{1P}$ is 0.26%. Theoretical and experimental values are all within 5% in high $\text{PS}_{5/2}$ region $0 \leq x \leq 5$. Although 29 NMR was not completed in lab, their theoretical units based off literature, and charge compensated from 31 P NMR, showed the presence of Si$^0$, Si$^2$, ESi$^2$, and Si$^{1Si}$ units. In addition to physical, thermal properties were determined. DSC was performed to observe thermal histories of LiSiPS. With increasing SiS$_2$ content from $x=0$ to $x=1$, $P^1$ transitions to $P^0$, and at the same time iSi$^0$ increases in concentration. Tg's and Tc's rose parallel to increasing NBS Si$^0$ and P$^0$ units, that is $x=0$ Tg/Tc=227/265 °C, $x=1$ Tg/Tc=312/348 °C. The MGFE was as well demonstrated showing a negative effect from increasing Tg's/Tc's on transition from $x=0$ to $x=1$. 
BIBLIOGRAPHY


ACKNOWLEDGEMENTS

I thank Dr. Steve W. Martin for giving me the opportunity to work in his lab with effective tools for studying materials properties and applications. He runs a first class organized facility with wonderful learning opportunities at every corner.

The Glass and Optical Materials research group members played a critical role in my development in the group since I was a newcomer. I thank Josh Roth, Brittany Curtis, Alison Whale, Kwanghyun Kim, Melinda Hoyt, Peter Enz, Deborah Watson for all instrumental and technical insights in glassy materials. In addition, I give special thanks to Steve Kmiec for assisting me in nearly every instrument, NMR, DSC, Impedance, XRD, Raman, and IR spectroscopy, and providing awareness into structural interpretations of my thesis.

I give thanks for my friends and family for supporting me through my graduate career. I am the first person in my family to obtain a graduate degree, and without my grandmother’s support throughout my entire academic life starting from Kindergarten, there is no way I could achieve this.