

## Neutron Scattering Studies of Lithium-Ion Diffusion in Ternary Phosphate Glasses

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### ABSTRACT

We have studied the diffusion mechanism of lithium ions in glassy oxide-based solid state electrolytes using elastic and quasielastic neutron scattering. Samples of  $x\text{Li}_2\text{SO}_4-(1-x)(\text{Li}_2\text{O}-\text{P}_2\text{O}_5)$  were prepared using conventional melt techniques. Elastic and inelastic scattering measurements were performed using the triple-axis spectrometer (TRIAx) at Missouri University Research Reactor at University of Missouri and High Flux Backscattering Spectrometer (HFBS) at NIST Center for Neutron Research, respectively. These compounds have a base glass compound of  $\text{P}_2\text{O}_5$  which is modified with  $\text{Li}_2\text{O}$ . Addition of  $\text{Li}_2\text{SO}_4$  leads to the modification of the structure and to an increase lithium ion ( $\text{Li}^+$ ) conduction. We find that an increase of  $\text{Li}_2\text{SO}_4$  in the compounds leads to an increase in the Lorentzian width of the fit for the quasielastic data, which corresponds to an increase in  $\text{Li}^+$  diffusion until an over-saturation point is reached ( $< 60\%$   $\text{Li}_2\text{SO}_4$ ). We find that the hopping mechanism is best described by the vacancy mediated Chudley-Elliot model. A fundamental understanding of the diffusion process for these glassy compounds can help lead to the development of a highly efficient solid electrolyte and improve the viability of clean energy technologies.

### INTRODUCTION

Recently, binary and ternary glassy oxide-based compounds have seen considerable attention for their potential as solid state battery electrolytes [1]. These glassy electrolytes have high ionic conductivity ( $\sim 10^{-3}$  S/cm) and low electronic conductivity attributed to their liquid-like, non-crystalline structure. These glasses are known for their high ionic conductivity at room temperature [1]. However, they do exhibit poor thermal stability at higher temperatures ( $< 500\text{K}$ ) which makes their application in high temperature devices questionable [1–3]. In order to mitigate this issue and increase the ionic conductivity even further the fundamental physics of the system needs to be better understood. The lithium ion ( $\text{Li}^+$ ) diffusion mechanism in these electrolytes is often difficult to determine because traditional bulk conductivity measurements do not easily distinguish between electronic and ionic conductivity. However, an understanding of the diffusion mechanism is vital to improve the glasses for commercial use. Neutron scattering is an established technique that allows us to study the migration and hopping mechanisms of lithium in these solids.

Various glass-ionic compounds such as  $\text{Na}_2\text{O}-\text{P}_2\text{O}_5$ ,  $\text{K}_2\text{O}-\text{P}_2\text{O}_5$  have been studied [4–6]. These compounds are known to have a base glass forming compound such as  $\text{P}_2\text{O}_5$ , which has

long been known to form polymer-like chains of PO<sub>4</sub> tetrahedra [4, 7]. These polymer-like chains serve to increase the volume of the glass and provide non-bridging oxygen atoms for Li<sup>+</sup> to diffuse between. The Li<sup>+</sup> are introduced to the glass by adding a Li<sub>2</sub>O modifier which serves to lower activation barriers for diffusion [8]. The addition of the Li<sub>2</sub>O causes a mixed anionic effect in the system, which also serves to increase Li<sup>+</sup> diffusion [9]. In order to further increase the ionic conductivity of the system a salt such as Li<sub>2</sub>SO<sub>4</sub> is added to increase the number of charge carriers and it is known that the SO<sub>4</sub> ions edit the macromolecular structure of the system [4-6, 10, 11].

Extensive characterizations have previously been done on the xLi<sub>2</sub>SO<sub>4</sub>-(1-x)(Li<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub>) system by various researchers. These have included electronic conductivity [5-6], Raman spectroscopy [4], and x-ray diffraction [2, 6]. It has been suggested that the microscopic structure is best described by the cluster-tissue model of glasses [12-13]. It has also been shown that the conductivity of the system goes down when the percentage of Li<sub>2</sub>SO<sub>4</sub> is greater than 60%, which also corresponds to initial signs of crystallization. In this study we aim to connect the lithium dynamics in these systems with their underlying structure on a microscopic scale using neutron scattering techniques.

## EXPERIMENT

The samples used in this study were prepared in pellet form and subsequently crushed into powders for the neutron scattering experiments. Four samples of xLi<sub>2</sub>SO<sub>4</sub>-(1-x)(0.5Li<sub>2</sub>O-0.5P<sub>2</sub>O<sub>5</sub>) with x=0, 0.05, 0.5, 0.6 were synthesized from Li<sub>2</sub>SO<sub>4</sub>, Li<sub>2</sub>CO<sub>3</sub>, and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> using a conventional melt-quenching method as outlined in [2, 6].

Quasielastic and elastic mean-square displacement measurements were performed on the High-Flux Backscattering Spectrometer (HFBS) [14] at the NIST Center for Neutron Research in Gaithersburg, MD. Samples were sealed with a lead seal in aluminum sample holders under a partial helium atmosphere. All samples were formed into an annular shape, wrapped in aluminum foil, to try to limit double scattering events. The HFBS was operated in two different modes 1) In elastic mode, elastic scans were conducted between 50K and 475K. 2) In quasi-elastic mode, measurements were performed between 50K and 450K with a minimum energy window of ±11 μeV or ±17 μeV. The accessible Q range covers 0.25 Å<sup>-1</sup> through 1.75 Å<sup>-1</sup> with 16 different detectors. The data was subsequently analyzed using the DAVE software package [15].

Diffraction measurements were performed on the same samples on the triple-axis spectrometer (TRIAx) at the University of Missouri Research Reactor Center. A collimation of 60°-60°-80°-80° was used with the PG004 reflection on the monochromator and the PG002 reflection on the analyzer. All elastic measurements were performed at room temperature under ambient pressure with 70 meV neutrons.

## DISCUSSION

### Structure

Previous work has been performed on samples with no Li<sub>2</sub>SO<sub>4</sub> (x = 0) in order to study the effects of varying the Li<sub>2</sub>O content [16]. It was demonstrated that an intermediate range order is formed by the P<sub>2</sub>O<sub>5</sub>, whereby P<sub>4</sub>O<sub>10</sub> molecules form the basis for a pseudo-BCC molecular crystal. It was also shown that the P<sub>2</sub>O<sub>5</sub> forms into polymer like chains when modified by an

alkali-oxide. This pseudo-BCC lattice has reflections that show up in our diffraction data shown in Figure 1. In particular, we are able to index the (110), (200), and (310) reflections, corresponding to  $1.19 \text{ \AA}^{-1}$ ,  $1.68 \text{ \AA}^{-1}$ , and  $2.66 \text{ \AA}^{-1}$ , respectively. Since the system is amorphous, these are diffuse peaks and are quite broad.

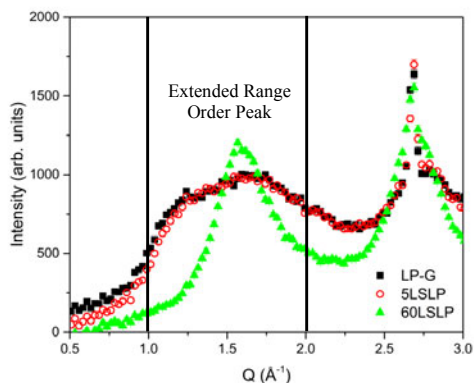


Figure 1: Elastic neutron scattering patterns at room temperature for the 0%, 5%, and 60%  $\text{Li}_2\text{SO}_4$  samples. The lines are purely guides to emphasize the extended range order peak.

The first peak shown in the diffraction data, between  $1.0 \text{ \AA}^{-1}$  and  $2.0 \text{ \AA}^{-1}$ , corresponds to the extended range order of the system. The 0% and 5%  $\text{Li}_2\text{SO}_4$  samples show a double extended range order peak, the first of which is not observed for the higher  $\text{Li}_2\text{SO}_4$  content sample. A clear alteration of the structure is observed, possibly reducing the size of clusters or modifying the base molecular units, but the basic pseudo-BCC structure is preserved.

Previous work has shown that the addition of  $\text{Li}_2\text{SO}_4$  edits the structure in such a way that it begins to resemble the cluster-tissue model of glasses [12-13]. The clusters would be made up of a similar structure as the  $x=0$  sample, with the local  $\text{LiPO}_3$  structure, while the tissue would consist of an amorphous mix of all the constituents. Features from the cluster-tissue model are not expected or observed in our data. We understand our results in the context of the cluster-tissue model, although the processes that we observe occur on a shorter length scale within the clusters.

## **Dynamics**

The diffusion mechanism of  $\text{Li}^{+}$ 's was studied via quasielastic backscattering. The quasielastic scan for the 50%  $\text{Li}_2\text{SO}_4$  sample is shown in Figure 2a and Figure 2b shows the Lorentzian width for all the samples with respect to the amount of  $\text{Li}_2\text{SO}_4$ . As shown in Figure 2b, there is a gap in data between 5% and 50%. Long counting times limited the number of samples that could be tested, but future studies will show whether the increase in quasielastic width is monotonic across the composition range or not. The quasielastic scan shown is a combination of all the  $Q$  values available to the instrument and were fit using resolution data taken on the 5% sample convolved with a delta function and a Lorentzian. It is clear from the

quasielastic data in Figure 2 and the mean-square displacement in Figure 3 that the width of the Lorentzian increases with  $\text{Li}_2\text{SO}_4$  content, which corresponds to an increase in diffusion.

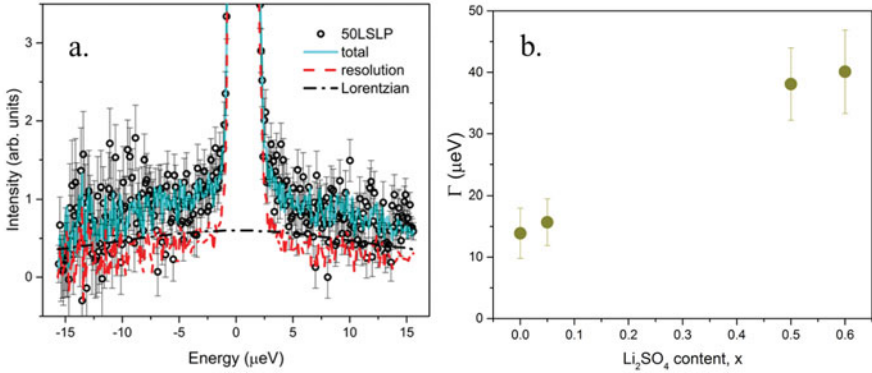


Figure 2: (a) Quasielastic fitting for 50%  $\text{Li}_2\text{SO}_4$ . (b)  $\text{Li}_2\text{SO}_4$  content versus Lorentzian width. Note, the Lorentzian width is for a combination of all available  $Q$  values. Both panels represent data taken at 450K. Error bars throughout the text represent one standard deviation.

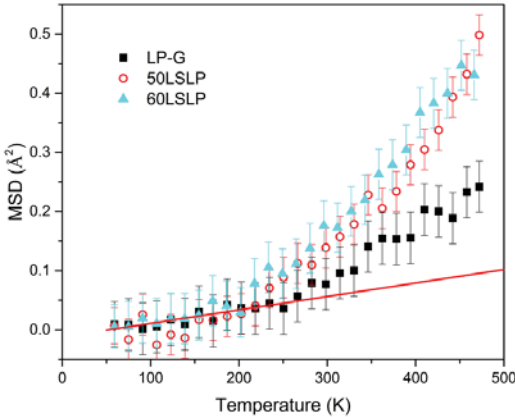


Figure 3: Mean-square displacement of all the samples. The red line signifies the slope from the Debye-Waller factor.

Figure 4 illustrates the  $Q$  dependence of the quasielastic width  $\Gamma$  for the  $x = 0.5$  sample. The scattering data in this sample does not suggest a simple isotropic diffusion model, but instead supports the vacancy-mediated Chudley-Elliot model (vmCEM) as shown below [17].

$$\Gamma = \frac{2}{\bar{\tau}Z_{enc}} \left[ 1 - \sum_{r_m} W_{enc}(\vec{r}_m) \cos(\vec{Q} \cdot \vec{r}) \right]$$

Here  $\bar{\tau}$  is the mean residence time,  $Z_{enc}$  is the number of atomic jumps per encounter,  $W_{enc}$  is the probability to make a jump, and  $\vec{r}$  is the jump length. As necessary simplifications in applying the model, it was assumed that the probability to make a jump is unity and the mean

residence time was combined with the number of atomic jumps per encounter as a scaling constant, since they are not known.

The standard Chudley-Elliott model assumes that a liquid close to its melting point has a locally lattice-like structure. The motion of the atoms in these glassy solids are oscillatory as is the case for regular solids. However, the randomness of the process and the high density of vacancies leads to an occasional jump into a neighboring lattice site. The vmCEM differs in that it allows for lower concentrations of vacancies and allows successive jumps to be correlated.

The specific Q-value data for each sample is shown in the inset of Figure 4. The interesting phenomena shown is that the jump distances stay roughly the same, the amplitude of the function that changes. This indicates that the diffusive jump observed in our energy window is independent of the observed structural alteration seen in Figure 1, but that more vacancies become available with an increase in  $\text{Li}_2\text{SO}_4$ .

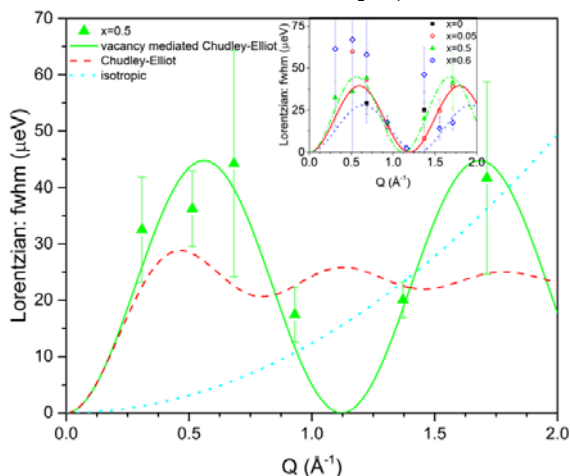


Figure 4: The separated Q-value data for the 50%  $\text{Li}_2\text{SO}_4$  sample, along with the comparison to an isotropic diffusion model and the standard Chudley-Elliott model. The inset shows analogous plots, without the comparison, for the other compositions.

## RESULTS

We have shown that an increase in  $\text{Li}_2\text{SO}_4$  serves to increase the amount of diffusion happening by a change in the structure of the system, along with some contribution from adding more lithium. However, the diffusion is happening along the same length scales independent of the structural change, but is still increased with an increase in  $\text{Li}_2\text{SO}_4$ . This increase is certainly in part due to an increase in charge carriers, but also may be due to sulphate ions lowering the energy barrier for diffusion by replacing phosphorus in parts of the chain. This is corroborated by the fact that the “allowed” jump distances we observed is  $\sim 4\text{--}6\text{\AA}$ , which corresponds to the length of the pseudo-BCC lattice formed by the phosphate chains. These phosphate chains seem to be the base structure of the system that facilitate diffusion, while the sulphate modifies the structure to allow for more diffusive jumps. Further investigation into exactly where the sulfate sits in the glass structure is needed, which will include the study of samples between the 5% and

50% compositions. In addition, an understanding of the microscopic energetics of the diffusion dynamics can provide direction on how to further increase diffusion.

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