SPS Chapter Research Award Final Report

<table>
<thead>
<tr>
<th>Project Title</th>
<th>Ionic Conductivity of the Lithium Clustering Effect</th>
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</thead>
<tbody>
<tr>
<td>Name of School</td>
<td>Coe College</td>
</tr>
<tr>
<td>SPS Chapter Number</td>
<td>1255</td>
</tr>
<tr>
<td>Total Amount Awarded</td>
<td>$2,000.00</td>
</tr>
<tr>
<td>Total Amount Expended</td>
<td>$2,000.00</td>
</tr>
<tr>
<td>Project Leader</td>
<td>Anne Ruckman</td>
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</table>

Abstract

The Coe College SPS Chapter will investigate the lithium clustering effect on silicate and borate glasses for better understanding the ionic diffusion due to electric fields and ionic conductivity. SPS members will learn how to prepare glass samples, conduct electrical impedance spectroscopy measurements, and witness the novel lithium clustering effect.

Statement of Activity

Overview of Award Activity

The main objective of this research was to develop a deeper understand the clustering effect of lithium in lithium borate oxide glasses, i.e. $x \text{Li}_2\text{O} \ (1-x) \text{B}_2\text{O}_3$, especially its effects on ionic conductivity. These glasses have been studied before, but very rarely with higher concentrations of lithium, due the difficulty of producing a homogeneous sample. Coe College Physics Department is well equipped to prepare such hard-to-obtain samples (up to $x = 0.67$), and during this last year acquired an impedance spectrometer – equipment necessary to measure the ionic conductivity.

Recent published works address the electrical properties and lithium diffusion of this glass composition by different methodologies such as Topological Constrains [Takeda, 2019], molecular dynamics [Varsamis, 2002; Vergiri, 2004] and Nuclear Magnetic Resonance [Montoliouit, 2019] but rarely on physical samples with $x > 0.5$. Scarce data can be found in the literature, but the data is relatively old [Tatsumisago, 1987; Yamashita, 1990; Chowardi, 1996].

This research tested models proposed by recent works for glass compositions with a higher lithium concentration. The glasses were prepared successfully and the samples were used to evaluate the electrical properties via Electrical Impedance Spectroscopy (EIS), the thermal properties via Differential Scanning Microscopy and the atomic structure via Raman, X-ray diffraction and Nuclear Magnetic Resonance.
The project was a bit more complex than anticipated with regard to glass production in samples containing more than 0.3 lithium content. Several samples were reproduced due to the detection of crystal formation or mechanical instability in the pelleting process.

This work contributed directly to the international understanding of charge carrier mobility in lithium borate systems. Our researchers developed a model to explain the unusual behavior of the ionic conductivity in these glasses, from the previously published weak electrolyte model.

Our SPS Chapter expanded our understanding of glass properties, exposed us to novel conductivity testing methods and analysis, as well as strengthened the department’s relationship with the Glass and Optical Research Group, part of the Materials Science and Engineering Department, at Iowa State University (ISU).

- Dr. Steve Martin’s Talk – More than 25 SPS members and 5 non-members attended Dr. Martin’s seminar on electrical properties of glasses. All participants networked and discussed graduate school research with him during breakfast and lunch.
- Wataru Takeda – Completed his mathematical model of the ionic conductivity of lithium borate systems, and submitted his publication
- Martha Jesuit – Completed the initial creation of the glass samples
- Graham Beckler & Will Guthrie – Completed training and are characterizing glasses
- Seth White & Ethan Weber – Completed training and are melting and running MD simulations on borate systems
- Anne Ruckman – Characterized glass samples and directed SPS research and participation
- Dr. Caio Bragatto – Trained, instructed, and led SPS researchers through the glass forming process and analysis
- Four experienced SPS researchers introduced and trained 4 underclassmen in advanced glass production techniques and ionic conductivity analysis
- Dr. Caio Bragatto’s Talk – 10 Coe College SPS Chapter members toured Iowa State University’s Materials Science and Engineering Department. All members participated in a lunch with 5 current PhD students in Dr. Martin’s group. Conversation topics included: what to look for in a graduate program, methods to select a principle investigator, life as a graduate student, and good research practices. Dr. Bragatto’s group held a joint research meeting with Dr. Martin’s group to further the SPS collaboration.

**Description of Research - Methods, Design, and Procedures**

Glasses were prepared by mixing adequate proportions of Li₂CO₃ and H₃BO₃ powders with over 99.5% purity from Sigma Aldrich. After 15 minutes of melting at 1000 °C in a platinum crucible, drops of melt were plate-quenched for values of x between 0.1-0.5 and fast-quenched at all higher concentrations. Rapid cooling methods minimized crystallization by roller-quenching glasses between two full metallic cylinders. All glasses were crushed into a fine powder with a mortar and pestle.

The sample’s structural properties were studied using differential scanning calorimetry, x-ray diffraction, Raman spectroscopy, and nuclear magnetic resonance. DSC was run from room temperature to 600 °C at a pace of 10 K/min using a Perkins-Elmer Diamond differential scanning calorimeter (DSC). To obtain the glass transition temperature the regression lines method was used. X-ray diffraction (XRD) measurements of powdered glasses verified the amorphous state of these structures. For that, a Bruker D8 Discover XRD was operated on 0.30-0.50 grams of each glass powder composition between 10-70° in 0.50° steps with 96 second time steps at room temperature. Raman spectra were obtained using a Jasco NRS-3100 Laser Raman Spectrometer, operated at 784.68 nm lines of an infrared laser which served as an excitation source for the Raman experiments. Nuclear magnetic resonance (NMR) was performed on powdered samples packed into zirconia MAS rotors with Kel-F caps. Sample mass was recorded from the difference before and after packing. A Bruker Avance Neo console using TopSpin 4.0 software applied a
constant magnetic field of 14.1 T. The N₄ fraction was obtained by integrating BO₃ across 23 ppm to 4 ppm and BO₄ across 4 ppm to -4 ppm. All samples underwent saturation-recovery to measure T₁ values. The ¹¹B T₁ relaxation speed increased with greater lithium content while total ¹¹B intensity decreased.

Electrical impedance spectroscopy was conducted in powdered samples compressed into pellets. The sample’s electrical response was obtained from a Gamry Instruments Interface 1010E Potentiostat/Galvanostat/ZRA impedance spectrometer. Impedance spectrometry applied excitation signals with 1500 mV across a frequency range of 1·10⁵ to 1 Hz.

**Discussion of Results**

The glass structure was in agreement with previous results from the literature, and most importantly followed the trend when the concentration of lithium was higher than typical values found in the literature, indicating that the glass was indeed homogeneous and behaving as it should. This is especially true for the NMR results, in which the experimental N₄ fraction results were in agreement with a well-established model published by Feller [Feller, 1982].

The same model is also used to predict the glass transition temperature (Tg). In this work, the Tg was obtained via DSC and in agreement with Bray’s model. Another way to predict the glass transition temperature was developed by Takeda [Takeda, 2019] using the Topological Constrain Theory. Although our Tg data was in agreement with Takeda, the expected ionic conductivity shows a disagreement with experimental results, both from previous work and the ones obtained during this one. Takeda’s work relates the number of free lithium ions, i.e. ions that are not attached to a cluster, to be proportional to the ionic conductivity of the material. Considering that the ionic conductivity is the movement of ions, this is a reasonable assumption.

![Figure 1 – Number of non-bridging oxygen (NBO) and logarithmic values of ionic conductivity as a function of the composition for the x Li₂O (1-x) B₂O₃ glass system.](image)

Since there is this discontinuity from Takeda’s model and experimental values, something else must be interfering with the ionic conductivity. Results by [Montolliout, 2019] suggest that what really controls the ionic conductivity of the glass is the number of non-bridging oxygen, which increase linearly when the ionic
conductivity reaches a plateau. Unfortunately, the work presents experimental data only up to $x=0.5$, the same composition where Takeda's model breaks from experimental results. In order to solve this, we propose that both works might be correct, but there is a different factor influencing the property. Borrowing from the weak electrolyte model, which assumes that the ionic conductivity depends on a dissociation equilibrium of charge carriers in the glass matrix [Ravaine, 1977], the linear increase non-bridging oxygen in the glass as a function of the lithium composition when $x>0.3$ keeps the dissociation of lithium ions constant, even when more lithium ions are added. This relation is better seen in Figure 1.

**Dissemination of Results**

Results from this work were presented as an oral contribution to the All-Iowa glass conference in 2019 and a poster has been submitted to the American Ceramic Society's (ACerS) Glass and Optical Division (GOMD) Annual Meeting in 2020.

The final draft of our research paper is nearly complete and will be submitted to the Journal of Non-Crystalline Solids during the first months of 2020.

**Bibliography**


Impact Assessment:

How the Project Influenced your Chapter

**SPS Influence:** Our SPS Chapter learned novel research techniques and gained experience on new equipment as well as enhancing our communication, teamwork, and problem-solving skills. We also strengthened relationships from first-year to senior undergraduates and faculty. When we encountered a challenge such as sample purity, mechanical formation, or time constraints, we discussed the potential barrier and divided the tasks into pairs with an expert researcher. This experience will influence future projects by combining molecular dynamics simulations with experimental research. Our SPS chapter will continue to investigate charge carrier mobility further in additional glass systems.

**SPS connection:** Our project created a connection with physics and engineering students at Iowa State University. We strengthened our relationships and assisted students in networking with Dr. Steve Martin and Dr. Caio Bragatto. Locally, Coe College SPS members learned safe, advanced practices for applied physics research while receiving support from their experienced mentors. Nationally, our chapter contributed to the scientific works and studies of lithium clustering at high concentrations. Our novel research addressed lithium borate glasses, but may be witnessed in additional glass systems.

**SPS Chapter Award Advice:** Our SPS Chapter would recommend investigating the proposed research field in detail by compiling as many references as possible. A complete literature review will minimize potential conflicts and guide the students as more challenges arise. We would also advise selecting a single faculty mentor for quick, and direct communication with additional faculty for support. Additionally, it is important to create and follow a project timeline to maintain progress and ensure overall success.

Key Metrics and Reflection

| How many students from your SPS chapter were involved in the research, and in what capacity? | 4 underclassmen and 4 upperclassmen served as computational and experimental researchers, over 25 SPS members attended Dr. Martin’s Talk, 10 SPS members visited ISU |
| Was the amount of money you received from SPS sufficient to carry out the activities outlined in your proposal? Could you have used additional funding? If yes, how much would you have liked? How would the additional funding have augmented your activity? | The budget was sufficient for our proposed research plan because it was supplemented with additional funding from external sources. Additional funding of $1000 would assist in travel costs for our 8 researchers to present their posters. |
| Do you anticipate continuing or expanding on this research project in the future? If yes, please explain. | Yes, we will investigate additional alkali systems |
| If you were to do your project again, what would you do differently? | We would plan for scheduling conflicts between research groups and within our department |

Press Coverage (if applicable)

This project was not covered by the media.
# Expenditures

## Expenditure Table

<table>
<thead>
<tr>
<th>Item</th>
<th>Please explain how this expense relates to your project as outlined in your proposal.</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>500g Lithium Carbonate with Shipping</td>
<td>Used to prepare the glass samples</td>
<td>$400</td>
</tr>
<tr>
<td>1kg Boric Acid with Shipping</td>
<td>Used to prepare the glass samples</td>
<td>$100</td>
</tr>
<tr>
<td>500g Silica with Shipping</td>
<td>Used to prepare the glass samples</td>
<td>$100</td>
</tr>
<tr>
<td>Poster Printing with Shipping</td>
<td>Primary method of disseminating the research project to the scientific community while the paper is under review as well as further students’ learning experience</td>
<td>$150</td>
</tr>
<tr>
<td>Light refreshments and notebook supplies for mentor/mentee introductory research meeting</td>
<td>Purchased supplies to follow best research practices and document experimental procedures and results</td>
<td>$150</td>
</tr>
<tr>
<td>Roundtrip travel from Coe College to ISU for glass analysis (at $0.545/mi reimbursement) for 3 cars</td>
<td>Around 15 members of our chapter visited Prof. Martin’s laboratories in Iowa State University, to learn more about electrical properties and glass research.</td>
<td>$300</td>
</tr>
<tr>
<td>Roundtrip travel from Coe College to ISU for Dr. Bragatto's talk (at $0.545/mi reimbursement) for 1 car</td>
<td>Travel reimbursement expenses for several samples to be tested at ISU</td>
<td>$100</td>
</tr>
<tr>
<td>Roundtrip travel from ISU for Dr. Martin's talk at Coe College (at $0.545/mi reimbursement) for 1 car</td>
<td>Assistance to host a well established glass conductivity researcher from ISU</td>
<td>$100</td>
</tr>
<tr>
<td>Lunch for 15 Coe College SPS members and supporting faculty during roundtrip traveling to ISU for glass analysis and lab tour</td>
<td>Lunch costs for Coe College SPS members touring ISU for the day and Dr. Martin’s researchers. This opportunity allowed students to ask questions about life as a graduate student and advanced research techniques</td>
<td>$300</td>
</tr>
<tr>
<td>Refreshments for 50 SPS members and faculty during Dr. Martin’s talk at Coe College</td>
<td>Refreshment assistance for students and faculty to attend Dr. Martin’s seminar on ionic conductivity in glasses</td>
<td>$275</td>
</tr>
<tr>
<td>Dr. Martin's meal expenses</td>
<td>Lunch cost for the guest speaker</td>
<td>$25</td>
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**Total of Expenses Covered by SPS Funding** $2,000

Coe College Student Senate funded Society of Physics Students provided $200 for the speaker Coe College Physics Department laboratory space, mixing supplies, and furnaces $500 Dr. Bragatto’s Laboratory Start-Up Research Funds $8,000 for the EIS and crucibles
Coe College SPS members and Dr. Caio Bragatto discuss life as a graduate student with Dr. Steve Martin’s research group after a laboratory tour at Iowa State University.
Dr. Steve Martin lectures on glass enabled solid state batteries at Coe College
Dr. Caio Bragatto instructs SPS member Will Guthrie to use the Electrical Impedance Spectrometer.

Coe College SPS members Seth White and Ethan Weber discuss their current progress at Dr. Bragatto’s weekly research meeting.
Coe College SPS member Graham Beckler compresses glass powder into aluminum lined pellets for conductivity testing.

Dr. Caio Bragatto with SPS members Anne Ruckman, Ethan Weber, and Will Guthrie at the completion of the SPS Chapter Research Award.