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Structural Analysis of Glass Materials using Raman Spectroscopy

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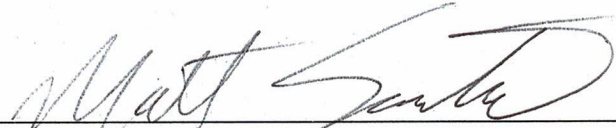
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Departmental Distinction in Biochemistry/Chemistry


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Structural Analysis of Glass Materials using Raman Spectroscopy

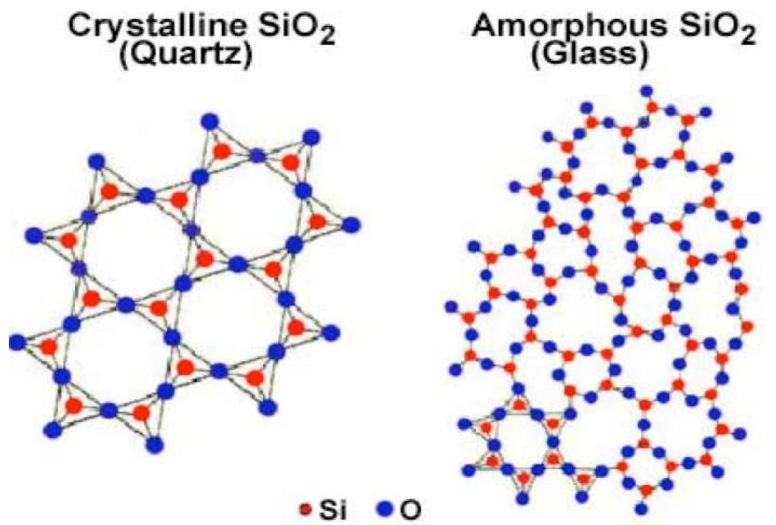
Abstract:

Glassy materials do not possess any long-range structural patterns, but are instead composed of numerous short-range structures. Raman spectroscopy was used to analyze the appearance of structural units in borate, silicate, and borosilicate glasses. By varying the mole fraction of modifiers, the effect of both modifier charge and size on the obtained spectra was observed. The Raman shift and peak intensity were used to analyze the insertion of the cation into the glass network. As the mole fraction of the cation increases, new peaks appear indicating the formation of new structural units that incorporate the cations. Heavier cations also appeared to have a greater influence on the glass network overall. Leaching of structural units in the network was performed through exposure to hydrochloric acid for various lengths of time. Raman spectroscopy was conducted to detect alterations to the glass network during the leaching process. The rate of precipitate formation during the exposures was used to determine the integrity of structural units. Changes in cation modifiers effect the rate of precipitate formation and integrity of the glass network due to the interaction between the cation and glass forming units. The effects of corrosive exposure over time are found to be dependent on modifier identity and modifier to former ratio by the results of this study.

Introduction:

Glassy material is frequently utilized in everyday applications around the world, and has been utilized for a significant time. With uses ranging from artistic to industrial, various compositions of glass networks have been developed to create a diverse range of both physical and chemical properties. Despite the extensive use of glassy materials, a lack of knowledge exists about

the structural patterns of the various glass networks that have been developed. Glassy materials are amorphous solids composed of a three-dimensional network that lacks both periodicity and symmetry^{1,3}. Glass networks, unlike crystalline solids, lack a long range structural pattern (figure 1). Instead, glass networks have a short-range

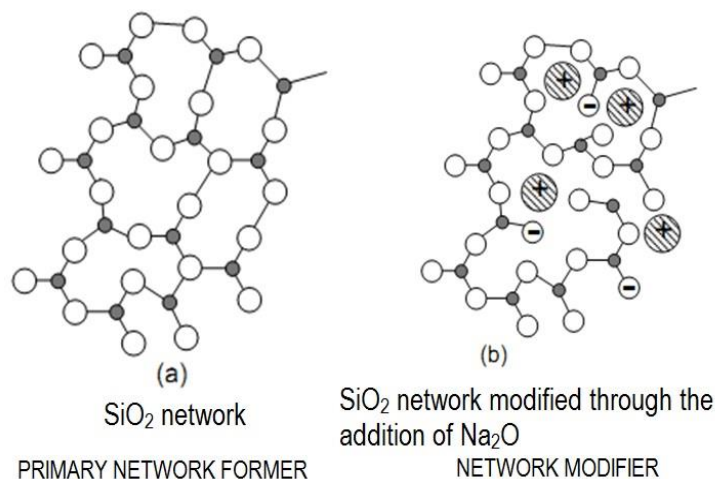


Solid State Structure,
www.ndeed.org/EducationResources/CommunityCollege/Materials/Structure/solidstate.htm

Figure 1. Comparison of glassy and crystalline solid structures

structure that is comprised of an uneven dispersion of multiple small structural subunits with ranges less than 50nm¹. The frequency with which particular structural units appear varies according to the composition of the glass and the method of synthesis.

There are two major components in a glass network, a former and a modifier. Formers create the small structural subunits that are necessary for the fundamental formation of all glass networks. Compounds commonly used as formers include oxides, such as silica (SiO₂) or phosphorous pentoxide (P₂O₅)⁴. In the course of this study, silica and boric acid (H₃BO₃) were used as the primary glass formers. Silica was used in the synthesis of silicate glass samples and boric acid was used in the synthesis of borate samples while a combination of silica and boric acid was used in the synthesis of a borosilicate glass. Silicate glass is the most commonly used glass former for commercial use⁴. Glass formers are the primary components to the glass network,



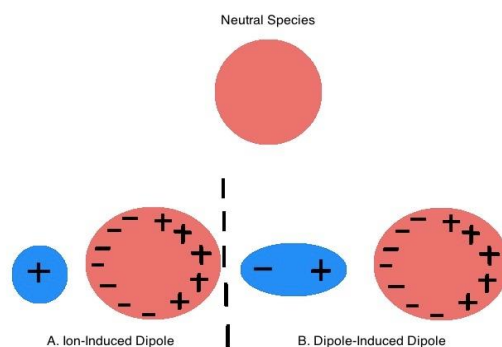
“SOLID STATE ELECTROCHEMISTRY.” *GLASSY ELECTROLYTE_1*, 1 Jan. 1970, solidstateelectrochemistry.blogspot.com/2012/10/glassy-electrolyte.html.

Figure 2. Comparison of a silicate glass network in the absence of a cation (left) and presence of a cation modifier (right)

however, the addition of modifiers to the network can change both the physical and chemical properties of the glass. Modifiers are typically cations, positively charged ions, that are incorporated into the structural subunits due to electrostatic interactions with the negatively charged oxygen of the structural unit (Figure 2)⁴. In this study, the cation used for modifiers include lead (Pb), lithium (Li), sodium (Na), potassium (K), rubidium (Rb), and cesium (Cs). Modifiers are useful for synthesizing glass that is specialized for a specific application, but the impact modifiers have on the structure of glass is unpredictable to some extent. The effects of modifier addition to a glass composition depends on the identity of the modifier, the identity of the former, and the ratio of modifier to former in the total glass composition. The alteration of the modifier to former ratio in the glass composition changes which structural units are most favorable in the glass network. Consequently the physical and chemical properties of the glass, such as color, brittleness, and integrity, are also altered. The unpredictability of glass networks beyond the short-range structure creates a fascination among the scientific community. The influences imposed upon a glass network through the addition of a modifier may be observed through spectroscopy techniques and qualitative analysis.

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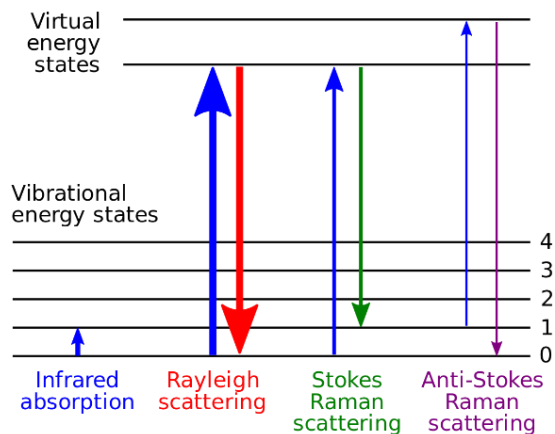
Raman spectroscopy is an investigative technique that utilizes laser light to fingerprint molecules based on their bonding patterns. Raman spectroscopy is a form of vibrational spectroscopy that utilizes the polarizability of a molecule to detect bonding interactions between atoms of an analyte^{2,5}. In order for a sample to be Raman active, the electron cloud of the analyte's atoms must be anisotropically polarizable⁵. In other words, the analyte must have an electron cloud



LENR Forum, 27 Nov. 2015, www.lenr-forum.com/forum/thread/2335-lenr-is-a-catalytic-process/.

Figure 3. Depiction of electron cloud distortion associated with molecular polarizability

capable of distortion (figure 3). Raman spectroscopy utilizes a laser to cause photoexcitation of an analyte, resulting in two potential types of scattering³. Upon contact with the analyte, a majority of the incident photons will be elastically scattered at the incident frequency of the laser, this is called Rayleigh scattering⁵. If the vibrations change the polarizability of the molecule, photons will be inelastically scattered, also known as Raman scattering⁵. The Raman scattering of the photons correspond to the vibrational energies of the molecule and can be categorized in two ways. Stokes scattering occurs when a molecule begins at a ground vibrational level and returns to a higher vibrational level after photoexcitation. Anti-stokes scattering occurs when a molecule in an excited vibrational state falls to a lower vibrational state after photoexcitation (figure 4). Stokes scattering produces a greater intensity on Raman spectra because it is more probable that a molecule will reside in the ground state initially due to the energetic favorability³. The frequency with which the incident photons are scattered back to the instrument after interacting with the analyte can be used to identify bonding patterns within the analyte.



“Raman Spectroscopy.” *Wikipedia*, Wikimedia Foundation, 29 Mar. 2018, en.wikipedia.org/wiki/Raman_spectroscopy

Figure 4. Representation of Rayleigh and Raman scattering that occur upon photoexcitation of an analyte

Raman spectroscopy is a relatively low-maintenance investigative technique. The technique can be applied to both liquid and solid samples and the presence of water in the environment does not affect the detection of the instrument. The lack of preparation necessary for quality results using this technique increases the simplicity and minimizes the expenses associated with analysis. However, there are some drawbacks of using Raman spectroscopy. Fluorescence, an emission of light that can result from photon absorption, may complicate analysis as it is capable of washing out a Raman signal⁵. Additionally, the radiation of the laser may lead to degradation of certain analytes over time.

Many glassy materials experience leaching, or deformation, upon exposure to corrosive environments². The principal mechanism for leaching is the removal of the cationic glass modifier. In general, the loss of this modifier markedly reduces the structural stability of the glass, leading to dissolution. Leaching is essentially a diffusion controlled ion exchange reaction in which the modifier is replaced by a cation that does not strongly bond with the glass former. By

systematically fluctuating the composition of the glass, an understanding of how changing the short-range structural units affects the leaching process was developed.

Methods:

Borate, silicate, and borosilicate glass networks were synthesized and then analyzed for they are commonly used in everyday applications. The components of each glass composition were measured and mixed in a platinum crucible. The amount of the former and the modifier in each sample was determined using a ratio that was created based on a balanced chemical equation for the sample (figure 2). In this study, silica (SiO₂) was used to synthesized silicate samples, boric acid (BH₃O₃) was used to synthesize borate samples, and a mixture of silica and boric acid was used to synthesize borosilicate samples. The primary modifiers used were lead and alkali metal cations. After being measured and mixed in the crucible, each sample underwent two heating cycles in a furnace to melt the sample. The temperature and length of time for each heating cycle varied between compositions. Typically, lead borate glass samples were heated at 1000°C for 10 minutes per cycle and lead silicate samples were heated at 1200°C for 15 minutes per cycle. Between each cycle the sample was cooled to room temperature and the mass was measured to ensure that the ratio of modifier to former was not disrupted in the heating process.

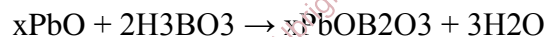
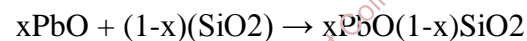


Figure 5. Schematic illustrating the representative methods for creating silicate and borate glasses. R can be varied from 0-35% and reliably obtain uniform glassy materials.

After two cycles of heating, the sample was poured onto an aluminum plate stored at room temperature and allowed to cool. If necessary, plate-quenching was used to expand the range of

glass formation. Plate-quenching allows the glass sample to cool more rapidly and solidify by trapping it between two aluminum plates. Plate-quenching can decrease crystallization of samples allowing for a greater range of compositions to be synthesized, however, sample obtained for by this method are too thin to perform acid test that measure integrity. Each sample was placed in a labeled envelope and stored in a desiccator after it was cooled to room temperature. It is crucial to store all borate samples in a water free environment to prevent the sample from reacting with the water and deteriorating.

Samples were analyzed using at B&W Tek Raman Spectrophotometer containing a 532 nm laser with 50 milliwatt power. Each spectrum was obtained using 100 percent laser power with varying acquisition time, fluctuating between 10 and 100s. A microscope attachment was used to hold the sample during analysis. A box was placed over the microscope attachment to create a dark environment for acquisitions. The creation of a dark environment prevented room light interference with the Raman signal and increased the quality of spectra obtained.

Acid tests were used to gain more information about the integrity and composition of glass networks. Samples were exposed to a corrosive material in an attempt to leach out specific structural components of the glass network. A 1M hydrochloric acid (HCl) solution was used for the leaching process. Two variations of acid tests were used in analysis. In a continuous acid test, the sample was placed in a 30 ml beaker and completely submerged in approximately 5 ml of 1M Hydrochloric acid solution for a set amount of time without disturbance. The length of exposure time for a continuous acid test varied from 10 minutes to 60 minutes. In a repetitive acid test, the sample was placed in a 30 ml beaker and was completely submerged in approximately 5 ml of 1M Hydrochloric acid solution, but was removed, rinsed, dried, and weighed in periodic increments. Typically, 4 minute increments were used for a repetitive acid test. The sample was carefully

removed from the Hydrochloric acid solution every 4 minutes using forceps, rinsed with water, gently dried with a kimwipe towel, and weighed on a balance before being placed back in the Hydrochloric acid solution. Prior to any acid test the mass of the sample was measured and used to calculate the percent mass retained of each sample throughout the acid test using equation 1. If any break in the sample was observed during the procedure of an acid test that compromised mass of the sample, no further acid tests were conducted using that sample.

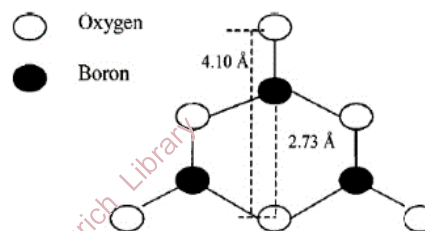
$$(1) \frac{\text{current mass of sample}}{\text{initial mass of sample}} \times 100 = \text{percent mass}$$

Additional analysis of the precipitate formed during the corrosion of acid tests was conducted using infrared spectroscopy (IR). Samples for IR were solid and crushed into a fine powder using a mortar and pestle prior to analysis.

Results and discussion:

In the Raman analysis of a pure borate glass, containing no modifier, only one peak was visible on the spectrum. The single peak at approximately 800 cm^{-1} corresponds to the boroxyl ring depicted in figure 6.

However, the intensity of this peak diminishes as the percent of modifier in the composition increases



Polarization Interactions and Boroxol Ring Formation in Boron Oxide from <https://www.princeton.edu/~flhs/paper258/index.htm>

Figure 6. Boroxyl ring structural unit

There are two major peaks that are consistently present in the Raman spectra of lead borate samples. These peaks are located at approximately 1300cm^{-1} and 1000cm^{-1} (figure 7). At 20 mole percent of lead modifier, the peak on the Raman spectrum that corresponds to the boroxyl ring has been reduced. It is important to note that the mole percent composition of lead modifier positively correlates

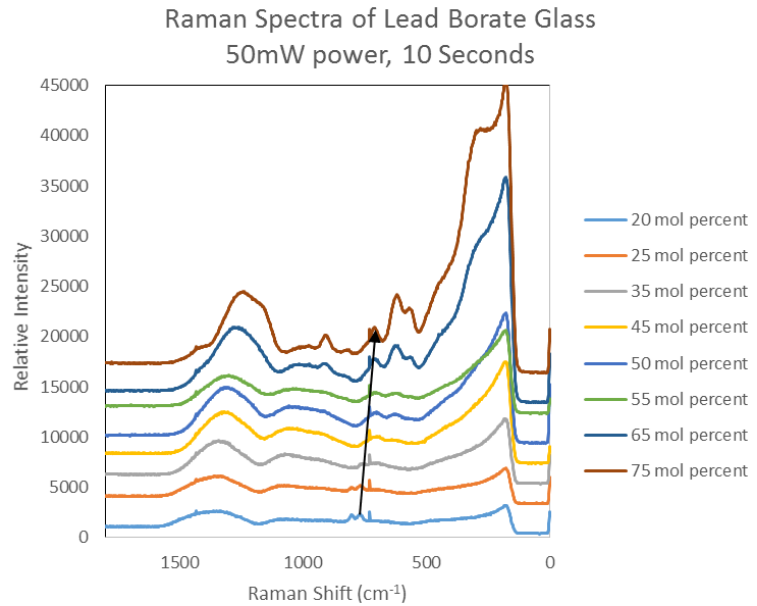


Figure 7. Raman spectra of lead borate glass with a composition ranging from 20-75 mol percent lead

with the appearance of new peaks on the Raman spectra. These new peaks are indicative of the presence of new structural units within the glass network. At this point in the study the identity of the structural units corresponding to these peaks is not known. As the percent composition of modifier increases, there is also an observable shift of the peaks located in the Raman spectra of lead borate glass. The peaks shift towards a lower wavenumber as the molar percent of lead increases (figure 7). Given that larger atoms tend to correspond to slower vibrational frequencies, it is suspected that the incorporation of lead, with a molar mass of 207.2 amu, into the borate network slows down the vibrational pattern associated with the lighter boron atoms, with a molar mass of 10.8 amu.

The Raman spectra of lead silicate glass samples contained one consistent peak at approximately 1000cm^{-1} (figure 8). As the mole percent of modifier is altered in the glass composition, minimal change is observed between the Raman spectra obtained. While the intensity of the peak at 1000cm^{-1} appears to increase with the addition of modifier, there is no noticeable shift in peak location. Due to the increased molar mass of silicon, approximately 28.1amu , compared to the molar mass of boron, it is hypothesized that the silicate structural units are able to better withstand the influences of the lead cation. The range of lead silicate samples analyzed was limited by the high melting point of silica and the maximum temperature of the furnace used for synthesis.

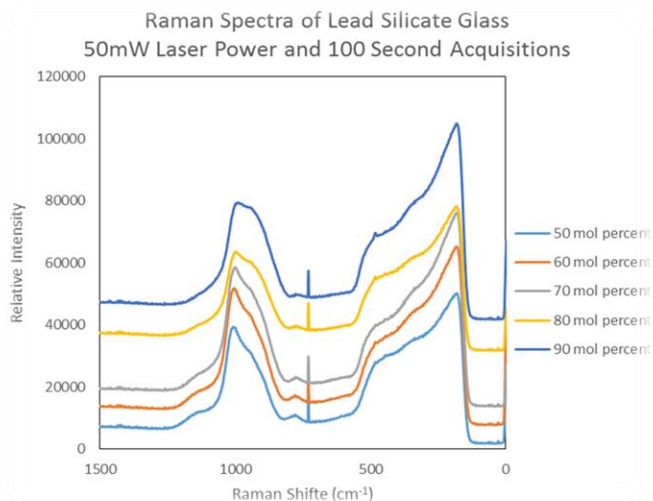


Figure 8. Raman spectra of lead silicate glass with a composition ranging from 50-90 mole percent

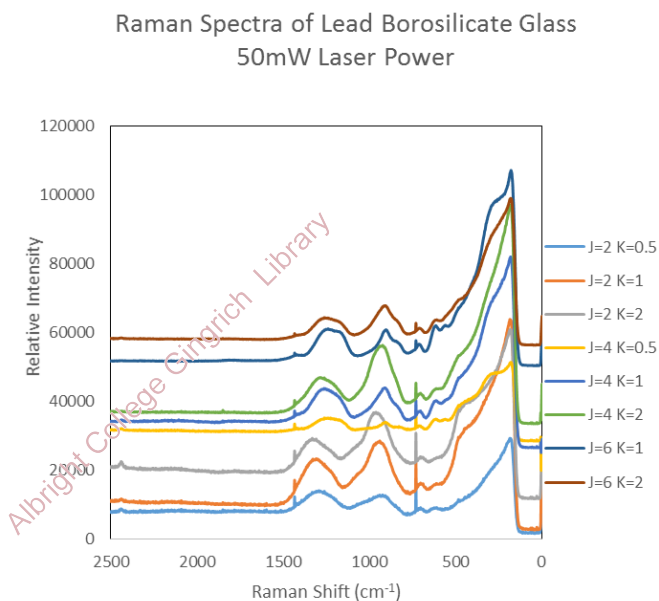


Figure 9. Raman spectra of lead borosilicate glass samples. J=lead modifier to borate former, K=Silica former to borate former

Lead borosilicate glass samples were synthesized using a mixture of borate and silicate formers. There are two primary peaks on the Raman spectra of lead borosilicates located at approximately 1000cm^{-1} and 1300cm^{-1} (figure 9). Minimal shifts are observed in these peaks as the ratio of modifier to formers and the ratio between formers is altered. As seen in figure 10, the two peaks that are present in the Raman

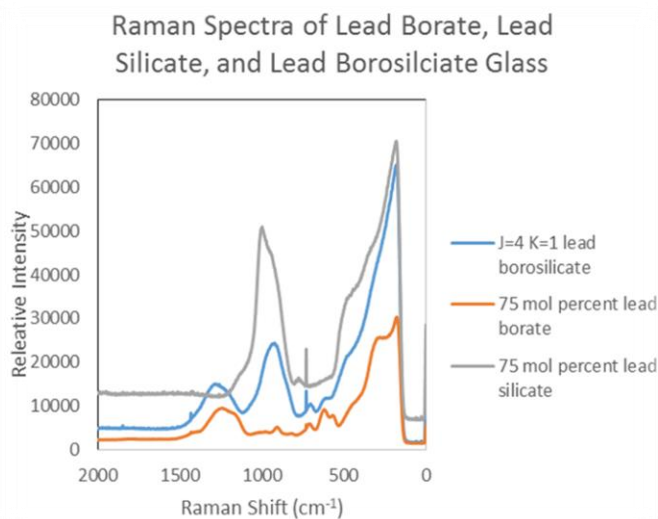


Figure 10. Comparison of Raman spectrum of lead borate, lead silicate and lead borosilicate samples

spectrum of a lead borosilicate samples correspond to peaks of the same frequency in the spectrum of lead borate (1300cm^{-1}) and lead silicate (1000cm^{-1}) spectra. The distinct correlation suggest that a borosilicate glass network is comprised of a combination of both borate and silicate structural units rather than a combination of new structural units that are unique to borosilicate glasses.

Analysis of the Raman spectra obtained from several borate glass samples with alkali metal cations revealed minimal variation between the spectrum of borate glasses containing alkali modifiers (figure 11a). The spectra obtained of each borate glass sample containing an alkali modifier was used as a reference during future acid tests. In figure 11b, a significant drop in peak intensity is seen between the Raman spectrum of a potassium borate preceding and following exposure to 1M Hydrochloric acid. Although no peaks of the potassium borate spectrum before acid exposure are lost after acid exposure, the change in peak intensity suggests that change is occurring structurally within the sample upon exposure to the corrosive substance.

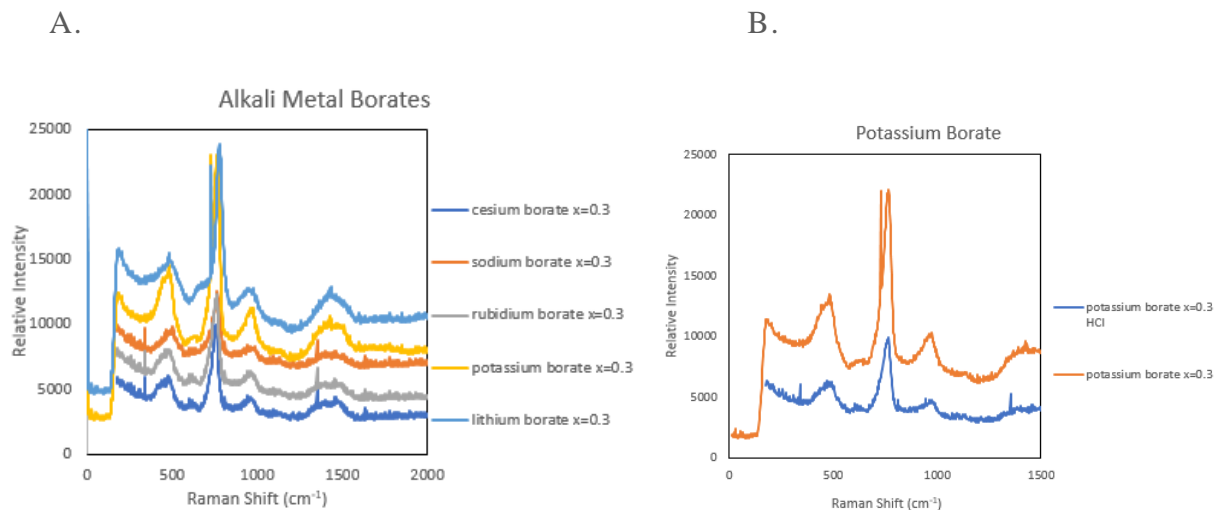
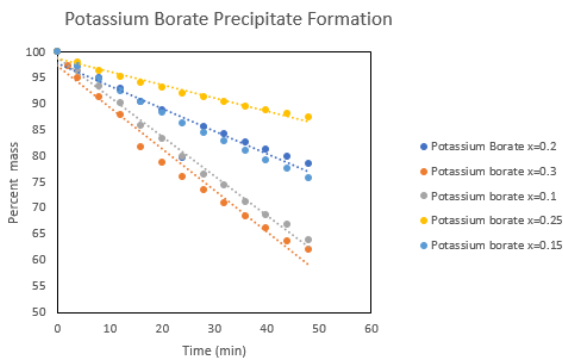


Figure 11. (a) Raman spectra of alkali borate glass samples (b) Raman spectra of potassium borate glass before and after exposure to 1M HCl

A repetitive acid test was conducted on each 0.3 mole percent alkali borate sample. As the molar mass of the modifier incorporated into the network, there was an observable increase in the rate of precipitation formation, or the rate of percent mass loss. Two explanations may potentially explain the correlation between the size of the modifier and the rate of mass loss. First, the increase in the rate of mass loss can be a result of the loss of the heavier cations that were incorporated into the glass network being removed from the glass network. If the modifier is stripped from the network early in the leaching process this hypothesis would be supported. Additionally, the increased rate of mass loss could be explained by and decrease in structural stability that is created by the incorporation of a larger cation into the glass network. At this point in time, the first explanation is hypothesized to be the primary cause of this phenomenon.

Due to the similarity of the alkali borate Raman spectra, one alkali modifier was chosen to be the model for additional acid tests. Potassium, located in the middle of the alkali group on the periodic table, was chosen because of its median molar mass and precipitation rate within the group. Multiple compositions of potassium borate were used, ranging between 0.1 and 0.3 mole percent potassium. The range of mole percent modifier was limited by the crystallization of the network. In the repetitive acid test of potassium borate, a decrease in the precipitation rate was observed as the mole percent of potassium modifier increased from 0.1 to 0.2. Originally, it was hypothesized that the increase in modifier content created a stabilizing effect on the glass network. However, as the molar composition of potassium was increased beyond 0.2 mole percent, no clear trend was observed in the rate of precipitation (figure 12a). After several repeat trials of the repetitive acid test on potassium borates samples, no consistent patterns could be observed. It is suspected that the shape of the glass sample is playing a larger role in the leaching process than anticipated. A significant decrease in rate of precipitate formation was observable in the results of a continuous acid test after approximately 20 minutes of exposure (figure 12b). It is hypothesized that the precipitate forms a protective barrier around the glass sample that prevents further leaching of the structural units.

A.



B.

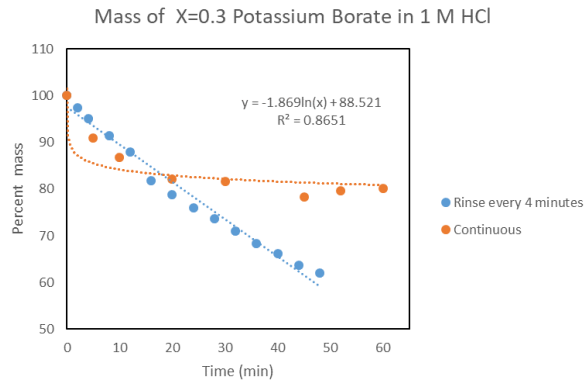


Figure 12. (a) Percent mass vs time for repetitive acid test of various potassium borate compositions using 1M HCl solution (b) Comparison of mass loss vs time for continuous and repetitive acid tests.

Repetitive acid tests were performed on borate samples containing cesium, potassium, sodium, lithium, or rubidium modifiers. In figure 13 it is noted that the rate of precipitation formation, or the percent of mass lost, over time decreases as the identity of the modifier moves up in the alkali group of the periodic table. As the atomic radius and molar mass of the modifying ion decreases, the rate of precipitation also decreases. The hypothesis that the

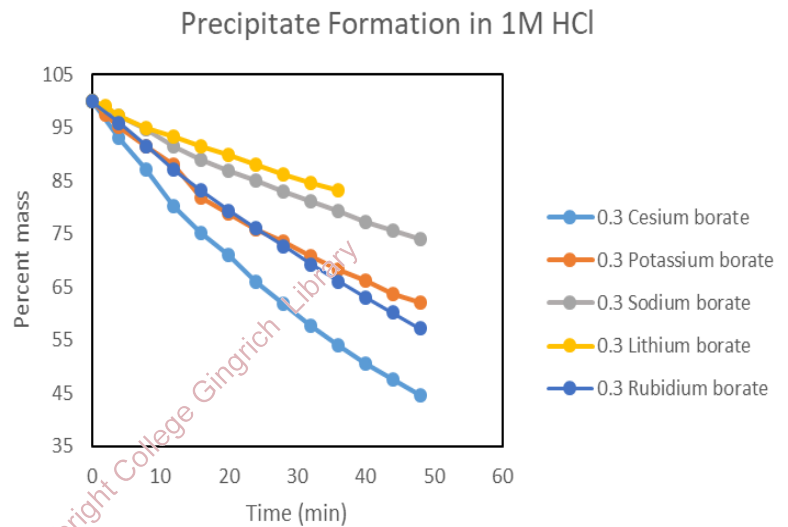


Figure 13. Comparison of precipitation formation for alkali borate glass samples using a continuous acid test with 1M hydrochloric acid

modifier is leached from the glass network first, is supported by the correlation between the modifier size and the rate of precipitation formation.

Infrared Spectroscopic (IR) analysis of the precipitate that resulted from lead borate glass upon exposure to 1M Hydrochloric acid was used to identify the precipitate composition. A comparison between the IR spectrum of the precipitate and the glass formers revealed a remarkable similarity. The precipitate was identified as boric acid, the former used for borate synthesis in this

Starting materials vs. Precipitate : Borate

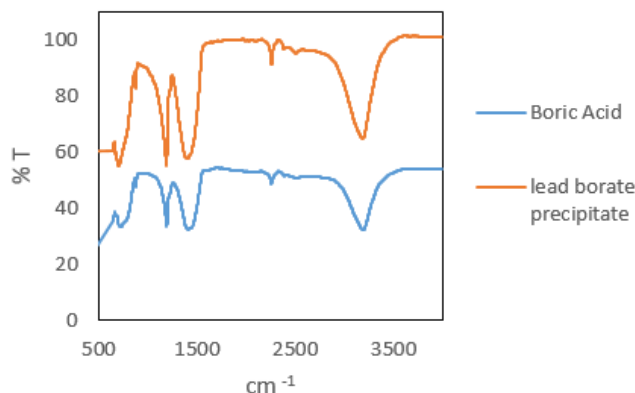


Figure 14. IR spectra of lead borate precipitate after exposure to 1M HCl and boric acid (H₃BO₃)

study. It is uncertain what is happening to the cation modifier during the leaching process at this point, but it is suspected that it may go into solution with the Hydrochloric acid. It is hypothesized that the cation is stripped from the network prior to degradation of the associated structural units.

In the future, atomic absorption spectroscopic analysis of the hydrochloric acid solutions used in acid tests may provide further insight into the leaching process. Currently, it is hypothesized that the cation modifiers of the glass network are in solution, but further analysis is necessary to confirm this hypothesis. Additionally, creation of a mold that can be used to control the shape and surface area during the synthesis of glass samples would be beneficial to the leaching process. Further analysis of Raman spectra will be necessary, in combination with the results of acid test, to identify further structural patterns in the glass networks observed.

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