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Investigation of tantalum sodium lead borate glass using laser ionization time of flight mass spectrometry (LITOF-MS)

Abstract

Laser ionization time of flight mass spectrometry (LITOF-MS) is a spectrometry method which can measure, with exceptional accuracy, the composition of ions within a glass system. Additionally, unlike other spectroscopy and spectrometry methods, this technique allows insight into the abundance of each kind of ion within a given glass system. This specific project tackled the topic of tantalum-doped sodium and lead borate glasses, as sodium and lead borate glasses doped with a transition metal is a topic which has not been thoroughly explored. Our group synthesized such a glass and was able to use LITOF-MS to gain insights into how the glass structure of said glass differs from conventional lead borate glass.

Keywords

laser ionization time of flight mass spectrometry, time of flight, TOF, LITOF-MS

I. Introduction

Within glass science, the glass structure of lead borate and sodium borate are particularly well understood and thoroughly researched. However, the ways in which transition metals interact with these systems when injected via doping are not. The aim of this project was to synthesize such a glass and gain insight into how the transition metal disrupts the glass structure. To this end, several tantalum lead borate glasses were synthesized and analyzed using laser ionization time of flight mass spectrometry (LITOF-MS). In order to properly comprehend said analysis, an understanding of both glass and LITOF-MS is required. Thus, a brief overview of both will be explored.

A glass is defined as, “an amorphous solid completely lacking in long range, periodic atomic structure, and exhibiting a region of glass transformation behavior” [1]. Regarding the first half of that definition, an amorphous solid is defined as being a solid with no lattice pattern. Specifically for a glass, there is no long-range periodic atomic structure, as outlined by the statement, “completely lacking long range, periodic atomic structure.” However, while there are no predictable long-range lattice patterns, there are some repeated small- and medium-range structures within the glass. It is these that can allow insight into how the overall glass is structured. Regarding the second half of that definition, “glass transformation behavior” can be defined using the definition of solids and liquids. In a liquid, molecules freely flow past one another, and therefore the structure can be described as amorphous. If this liquid can be cooled below its melting point without crystallization, it becomes a supercooled liquid. If this supercooled liquid is cooled further, to the point where the viscosity becomes too great, it becomes a solid and that solid is a glass. This is achieved by cooling the melt quickly enough, or

in another way such that there is no time for crystals to form. To examine the aforementioned medium-range atomic structures, one can use laser ionization time of flight mass spectrometry.

Laser ionization time of flight mass spectrometry (abbreviated LITOF-MS or simply TOF-MS) is a kind of spectrometry which can measure the mass and abundance of those medium-range ions within a sample. While a sample is held in a vacuum (equal to 10^{-7} mTor for our spectrometer), the spectrometer uses a low-powered laser (a Nd:YAG laser with a wavelength 266 nm for our spectrometer) to ionize said sample. After a section of the sample is ionized, an electric field is used to pull the ions towards a detector. The instrument measures the time between when the laser is fired to when the ions arrive at the detector. Because the speed of light is so fast, this measured time is used to approximate the time it takes for the ion to travel from the sample to the detector. To calculate the mass of the ion, the spectrometer takes the known distance between the sample and detector, the time it takes for each sample to reach the detector, and Newton's second law to calculate the mass of the ion. There is slightly more nuance to the system, but this is its basic functionality and is sufficient for this analysis.

To actually run a sample, said sample needs to be ground up and glued to a TOF tip, this tip is then meticulously inserted into the spectrometer in such a way that the vacuum is maintained. At this point the sample can be run. Because of the nature of this kind of spectrometry, only either the positive or negative ions could be examined at a given time. This means spectra of the ions can only ever be positive (in that they examined the positive ions) or negative (in that they examined the negative ions). During the beginning of this research period the negative ions were examined, and then halfway through the research period the spectrometer settings were changed to examine the positive ions.

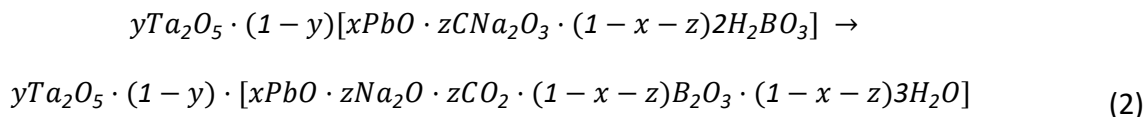
The benefits of using an instrument like LITOF-MS is that it not only identifies the ion but also indicates its abundance. Fig 1 shows an example of such a spectra, and here it is plain to see that some peaks are higher than others, indicating the ratio between the abundance of different ions. The actual identification of the peaks is something which is not included in the hardware or software of the TOF-MS, and therefore will not be discussed in this section, and for now this is a sufficient understanding of TOF-MS.

II. Methodology

In order to synthesize a glass, one must first have a glass in mind, create a chemical formula for said glass, and then finally create the chemical equation which denotes the reactants necessary to create the desired glass. Our goal was to synthesize a sodium lead borate glass doped with tantalum, and to that end we created equation 1 to describe our glass.

$$yTa_2O_5 \cdot (1 - y) \cdot [xPbO \cdot zNa_2O \cdot zCO_2 \cdot (1 - x - z)B_2O_3] \quad (1)$$

Where x, y, and z is a decimal from 0 to 1 and is proportional to the mol% of each compound. Using equation 1 as a product, we were able to create a chemical equation for our glass, as seen in equation 2.



After the chemical equation was created, a spreadsheet was created, and it contained the calculations needed to convert the chemical formula of the desired glass into grams of reactants. Also within the spreadsheet was the calculation of the weight loss of the sample. This is necessary

because some of the products of the reaction are expected to boil off, and our group measured this weight loss in order to ensure our melt was behaving as expected. All four chemicals needed for our reactants were purchased from Aldrich Chemicals. The lead oxide, sodium carbonate, and boric acid were all ultra high purity ($\geq 99.999\%$), while the tantalum was of high purity (99%).

Glass preparation -

The first step in synthesizing the glass was weighing the platinum crucible used to hold the reactants. Then, using the calculations done in the spreadsheet prior to sample preparation, each reactant chemical was weighed out and placed in a platinum crucible. All samples were 6g batches, with the sole exception of the 40 mol% Ta₂O₅ tantalum lead borate sample, explained in further detail in a following section. The crucible and chemicals were then weighed together, and the contents of the crucible were hand mixed using a metal instrument for five minutes. Next, the platinum crucible was placed in a furnace either at 1400°C or 1500°C depending on the specific sample. Most of the tantalum lead borate and tantalum lead sodium borates were cooked at 1500°C, while most of the tantalum sodium borates were cooked at 1400°C. The samples were first cooked for 15 minutes, and then taken out of the furnace to evaluate the weight loss of the contents and compare to the theoretical calculations. The samples were then put back into the furnace for an additional 15 minutes before being roller-quenched. The roller-quenching process involves pouring the still-molten sample through two metal wheels spinning at high speed. These wheels both rapidly cool the sample and shape the sample into 30-80 microns strips. These samples are then crushed into a fine powder using a mortar and pestle

before being glued onto a TOF (Time of Flight) tip. At this point, the sample is ready to be placed in the TOF spectrometer.

Using this technique, eleven tantalum-doped borate glasses were created. This includes six tantalum lead borate glasses, two tantalum sodium lead borate glasses, and three tantalum sodium borate glasses. Based on the chemical composition given in equation 1, the tantalum lead borate glasses were all made with an x value of 0.3 and a z value of 0, with the tantalum oxide concentration varying. The six tantalum lead borate glasses had y values of 0.05, 0.10, 0.15, 0.20, 0.25, and 0.40. With regards to the sodium lead borate glasses, both had y values of 0.20, however one of the glasses had an x and z value equal to 0.25 while the other had an x value of 0.1 and a z value of 0.4. Concerning the tantalum sodium glasses, all three had a z value of 0.4, and had y values of 0.10, 0.20, and 0.30. Below Table 1 is a table that contains the above information.

x	y	z	Glass Type
0.3	0.05	0	tantalum lead borate
0.3	0.10	0	
0.3	0.15	0	
0.3	0.20	0	
0.3	0.25	0	
0.3	0.40	0	
0.1	0.2	0.4	tantalum

0.25	0.2	0.25	sodium lead borate
0	0.1	0.4	
0	0.2	0.4	tantalum sodium borate
0	0.3	0.4	

Table 1. The above table shows all the tantalum borate glasses that were able to be synthesized, with the x, y, and z values corresponding to the x, y, and z seen in equation 1, and each had a value between 0 and 1. The three kinds of tantalum borate glasses that were the tantalum borate lead glass, the tantalum lead sodium borate, and the tantalum sodium borate glass. 6 tantalum lead borate glasses were able to be synthesized, 2 tantalum sodium lead borate glasses were able to be synthesized, and 3 tantalum sodium borate glasses were able to be synthesized.

Because of time constraints and technical difficulties, only the six tantalum lead borates were able to be run in both the positive and negative and properly analyzed. However, the positive spectra for the tantalum sodium lead borates and tantalum sodium borate glasses were able to be acquired.

Glass Formation Difficulties -

Unlike previous TOF experiments studying well-known glasses, this research focused primarily on tantalum lead borate glasses, a glass family which previously has had little to no research done on it. This is partly due to the difficulty in forming the glass. Tantalum lead borate glasses with tantalum oxide concentrations equivalent to 5 mol% to 25 mol% were able to be formed, but not without high temperatures and immediate roller quenching. The 40 mol% sample was only able to be formed by adding two 6g batches and two more 8g batches on top of each other. Because the initial 6g batch did not pour, as the melt was too viscous, another batch

with the same composition was added on top. After that sample also did not pour, a third batch was added atop. This time, however, rather than it being a 6g batch, it was an 8g batch. This was repeated for a final time, at which point the melt was able to be poured and a glass could be extracted.

It is for this reason that lead borate glasses with tantalum oxide concentrations of 30 mol% or 35 mol% were not made. While it likely is possible to make these samples, the process would be rather time-consuming and resource draining.

Taking data -

Because of the nature of TOF-MS, only positive or negative ions can be analyzed at a given time. Prior to running the negative or positive ions of the newly synthesized glass, an older, already existing sample of lead borate glass was used to calibrate the spectrometer to ensure that the spectra for positive and negative ions could be as accurate as possible. However, due to some technical difficulties with the spectrometer itself, towards the end of the research period the positive spectra were more noisy and were not able to be analyzed to the same extent as the negative spectra.

Regarding the running of each sample, this was done for each glass by mounting the TOF tip with the sample atop a rod and inserting it into the spectrometer. From here, the Nd:YAG laser was shot at the sample, the time of flight of the ions was recorded, and the program itself is a conversion between time of flight and size of ion in amu. Figure 1 is an example of what the resulting data looks like.

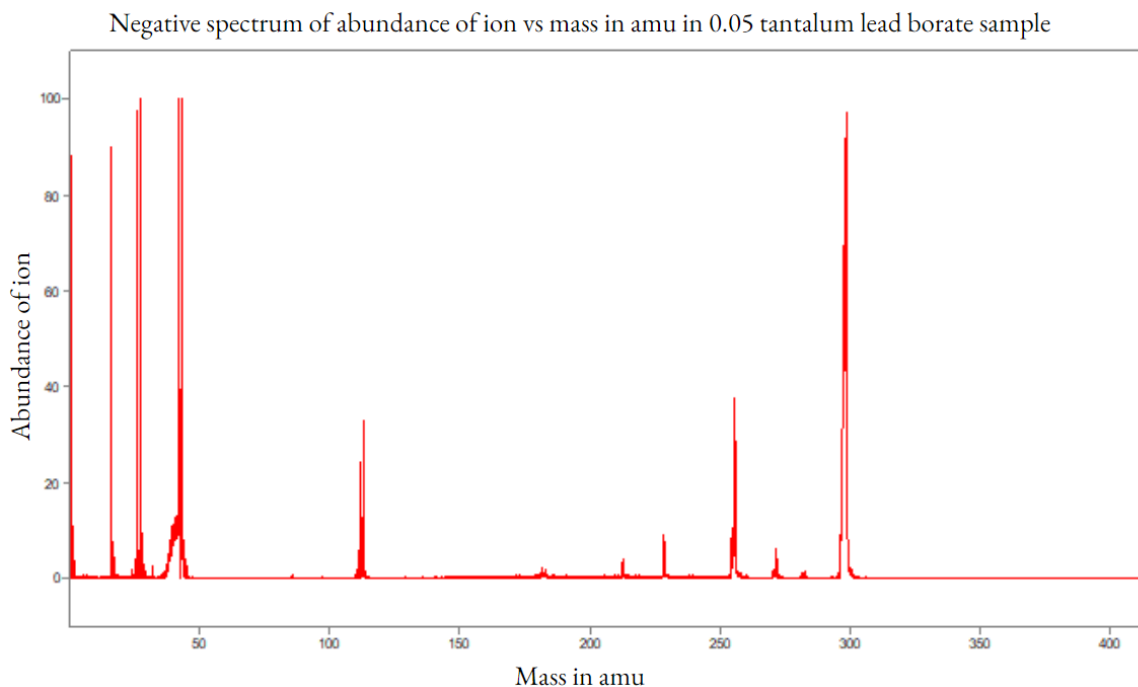


Figure 1. Example of a negative spectrum. This specific sample is a tantalum lead borate when $y = 0.05$, $x = 0.3$, and $z = 0$, ran at a gain of 400mV. The x axis is the mass in amu and the y axis is the intensity of the signal from a given ion of a given amu. The exact units of the y-axis depend on the gain of the spectrometer in addition to other settings of the spectrometer, but the height of the peak is proportional to the abundance of what that ion represents.

Each sample was run several times at different gains, with each run being saved separately. “Gain,” in this context, can be thought of as the scaling of the y-axis of each spectrum. Lower gain results in higher peaks but more noise, and higher gain results in less noise but lower peaks. Each sample was run with a gain of 100mV, 130mV, 160mV, 200mV, 250mV, 300mV, 400mV, 500mV, 630mV, 800mV, and 1.0V. Of these 11 runs, the three with the cleanest data were chosen to be exported and analyzed. Choosing the cleanest spectrum within the set of 11 was a subjective process based on the discretion of the researcher. This is both because the TOF-MS software does not have features which can mathematically determine which spectrum has the least amount of noise, and because the process of exploring the spectra to do the analysis on another computer is cumbersome. If time allowed a more thorough analysis of the noise present

in the spectra would have been conducted. All the spectra shown in this paper have a gain of 400mV.

The next step was to identify the peaks seen in the spectrum. This was done using IsoPro 3.0. This program, written by Mike Senko, takes any chemical formula for an ion and produces the corresponding TOF spectrum output using the known values of isotopes and their relative abundance. The three cleanest peaks were used to identify the peaks, and then once all peaks were identified, they were labeled. This yielded a new spectrum, an example of which is shown in figure 2.

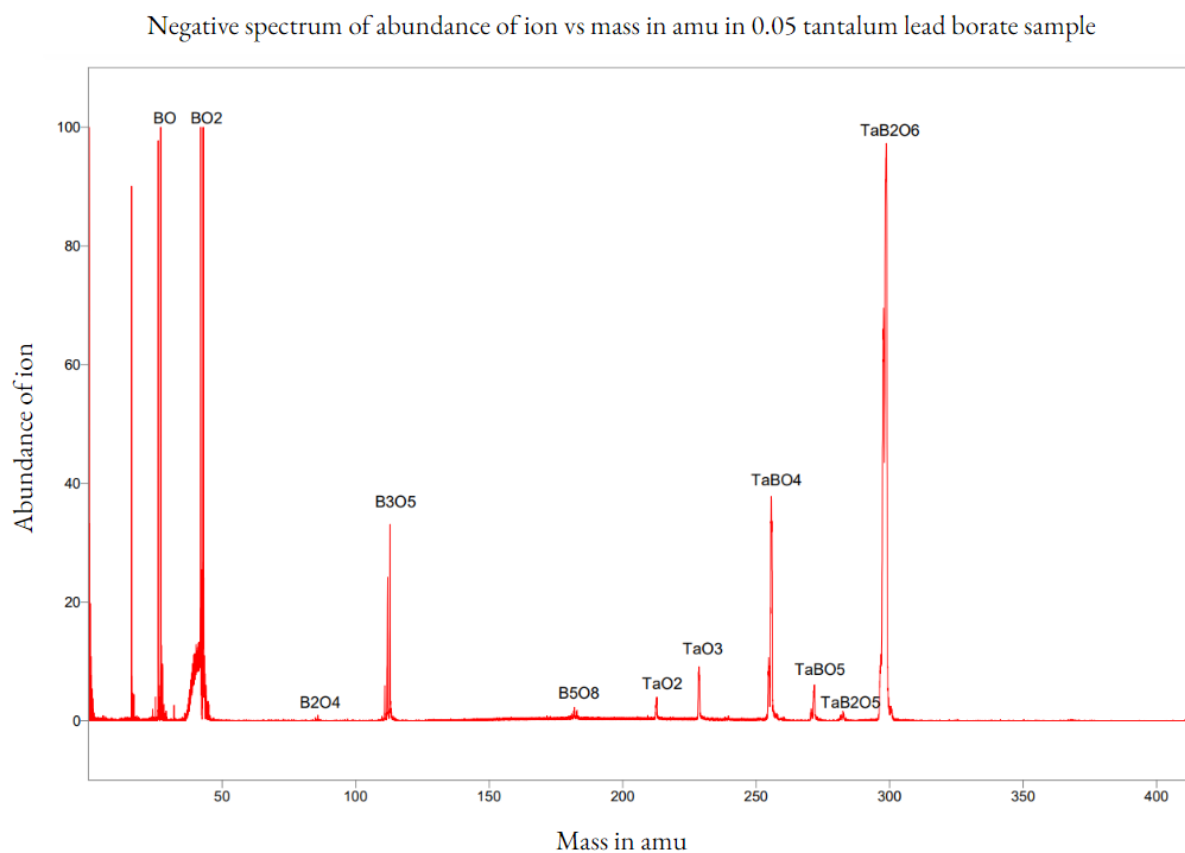


Figure 2. Negative spectra of tantalum lead borate glass with $y = 0.05$ run at a gain of 400mV with identified peaks. Like with figure 1, this chart has x-axis units of amu, and y-axis units dependent on the gain and other settings of the spectrometer. The peaks and their corresponding identification can be found in table 2.

III. Results and Discussion

Due to time constraints, only the tantalum lead borate glasses were able to have their peaks identified. The tantalum sodium lead borate and tantalum sodium borate glasses had their positive spectra taken, but the peaks were not identified nor analyzed. The peaks identified on the tantalum lead borate spectra (both positive and negative) are shown below. Table 2 are compounds found in the negative spectra, while table 3 contains the compounds seen in the positive spectra. Due to time constraints, only the negative spectra were able to be analyzed beyond the identification of peaks, and as such the analysis and discussion will largely focus on those peaks and spectra.

Peak (amu)	Compound Assignment	Peak (amu)	Compound Assignment
26-27	BO	180	Ta
42-43	BO ₂	197	TaO
74-75	BO ₄	204-209	Pb
84-86	B ₂ O ₄	213	TaO ₂
110-113	B ₃ O ₅	239-240	TaBO ₃
213 (-215)	TaO ₂	246-251	PbBO ₂
229	TaO ₃	410-417	Pb ₂
255-256	TaBO ₄	426	Ta ₂ O ₄
271-272	TaBO ₅	428-433	Pb ₂ O
280-282	TaB ₂ O ₅	443	Ta ₂ O ₅
296-299	TaB ₂ O ₆	454-460	Pb ₂ BO ₂

Table 2. Above are the peak identifications for the negative spectra of the tantalum lead borate glasses. The process of identification is described in the section above.

468-469	Ta ₂ BO ₆
471-476	Pb ₂ BO ₃
540-546	Pb ₂ B ₃ O ₆
655-662	Pb ₂ B ₅ O ₁₂

Table 3. Above are the peak identifications for the positive spectra of the tantalum lead borate glasses. The process of identification is described in the section above.

Some initial observations include the absence of the PbO and PbB₃O₆ peaks, and the change in the relative ion abundance as the tantalum concentration increases. Regarding the PbO peak, while its absence may be significant, as it is present in typical lead borate samples, due to technical difficulties with the TOF spectrometer towards the end of the research period, the positive spectra were not as accurate. Therefore the absence of the PbO peak cannot be concluded to be the result of the sample itself, but instead may be due to fault on the spectrometer. However, the same cannot be said about the PbB₃O₆ peak.

The PbB₃O₆ peak, also referred to as the boroxol ring, is quite ubiquitous in other negative spectra of lead borate glasses [2]. Previous studies on lead borate glasses have consistently shown the presence of this ring and that on a TOF spectra, this corresponds to a peak at ~336 amu. Additionally, it was this peak that played a key role in calibration of the spectrometer at the beginning of the research period. Given that tantalum lead borate glasses fall under the lead borate glass family, one would expect to see this compound's presence. However, notably, all tantalum lead borate glasses lacked this ring, even when the tantalum oxide content is 5 mol%.

One possible explanation is that the intense heat with which the sample was cooked resulted in the rings not being able to form. Previous studies on lead borate glasses have usually cooked the glass at a temperature of 1000°C. Additionally when cooked at higher temperatures, past analyses have noticed the lead in the glass not well incorporating into the rest of the glass. Therefore, to see if the higher temperatures disallows the formation of this ring, a lead borate sample with the lead oxide concentration at 30 mol% was mixed and then fired at 1500°C (unlike the previous 1000°C of other lead borate samples) for 15 min before being prepared like all other previous samples. This sample, however, has yet to be tested due to technical difficulties with the TOF spectrometer. If the sample is run and it is shown that there are no boroxol rings, then that reinforces the hypothesis that the high cook temperature prevents the rings from forming. On the contrary, if the sample is run and there are still boroxol rings, then that would suggest that some other phenomenon is responsible. Finally, the last observation was regarding the regions of pure tantalum (specifically TaO_2 and TaO_3) within the glass and phase separation.

Regarding the presence of pure tantalum compounds and their relation to other borate compounds, it was observed that the intensity and prevalence of tantalum-boron compounds dramatically decreased as the tantalum concentration increased. Figure 3 is an overlay of the 5 mol%, 10 mol%, 20 mol%, and 40 mol% tantalum oxide concentrations with the B_3O_5 , TaO_2 , and TaB_2O_6 highlighted.

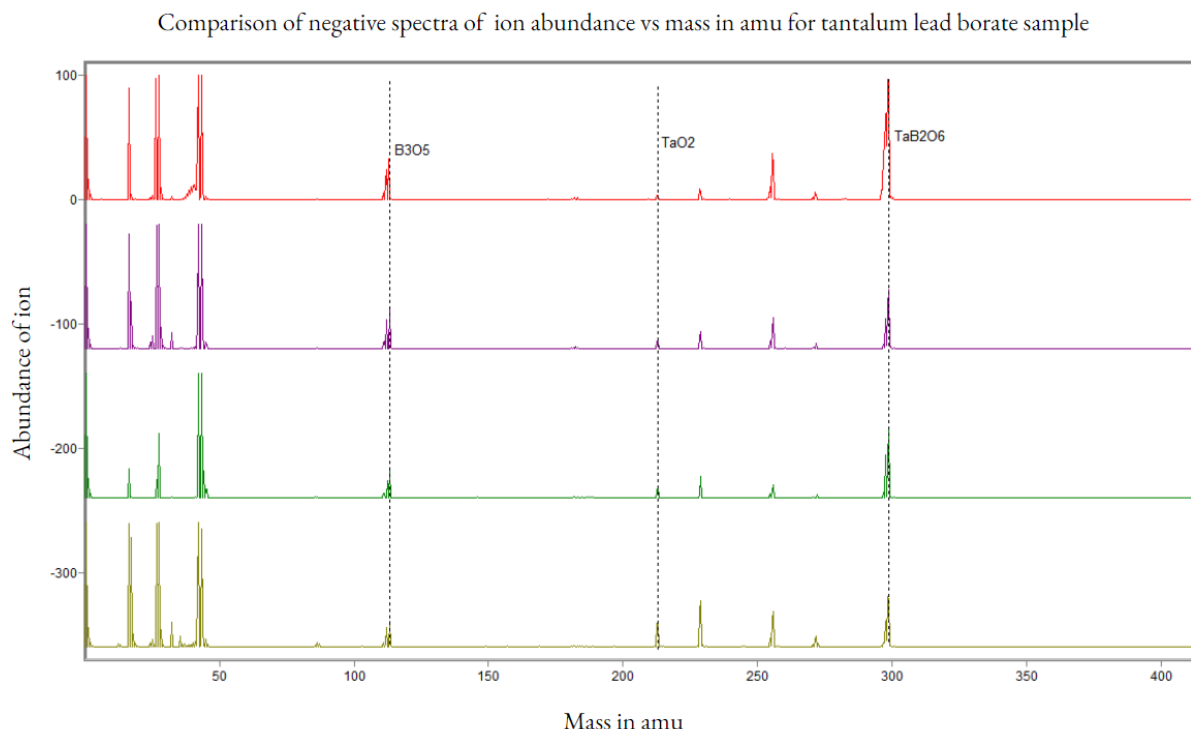


Figure 3. Four negative spectra of tantalum lead borate glass of different concentrations of tantalum overlaid with the B_3O_5 , TaO_2 , and TaB_2O_6 peaks highlighted. The x-axis is in amu, and the y-axis is intensity of peak, though because the peaks are overlaid, the purple, green, and yellow spectra are offset in the negative y direction. All are tantalum lead borate glasses but with different concentrations of tantalum. The red spectrum at the top represents tantalum concentration equal to $y = 0.05$. The purple spectrum represents a tantalum concentration equal to $y = 0.10$. The green spectrum represents a concentration of $y = 0.15$. The yellow spectrum represents a concentration of $y = 0.20$. All of the spectra were run at a gain of 400mV.

As demonstrated by the graphs, as the Ta concentration increases, the peaks containing boron decrease and the peaks containing tantalum increase. This is not unexpected. However, what is rather startling is the rate of decrease in the boron peaks, with TaB_2O_6 being the main peak exhibiting this behavior. By simply increasing the concentration by 5 mol%, from 5 mol% to 10 mol%, the intensity of this peak drops by 51.1% (from 97.2 to 47.5). Simultaneously, the pure tantalum oxide peaks (including TaO_2) dramatically increase. From 5 mol% to 10 mol% tantalum oxide, the TaO_2 increased by 57.8% (from 4.5 to 7.1). This trend increases until the tantalum oxide compounds are nearly equal to those tantalum-boron compounds in intensity.

While initially startling, after some analysis this sharp increase is explained by how the glass composition is set up. Using equation 1, one can determine the ratio of borons to tantalums. This is valuable because it allows us insight into how many boron atoms are available to bond with the tantalum. That ratio can be seen in equation 3.

$$\frac{0.7(1 - y)}{y} \quad (3)$$

Where y is simply the tantalum oxide mol%. When this equation is plotted, it demonstrates why the tantalum-boron compounds decrease rapidly, and why the tantalum oxide compounds increase rapidly. Figure 4 is just such a graph, with the tantalum oxide concentrations of 5 mol%, 10 mol%, 20 mol%, and 40 mol% highlighted by dots.

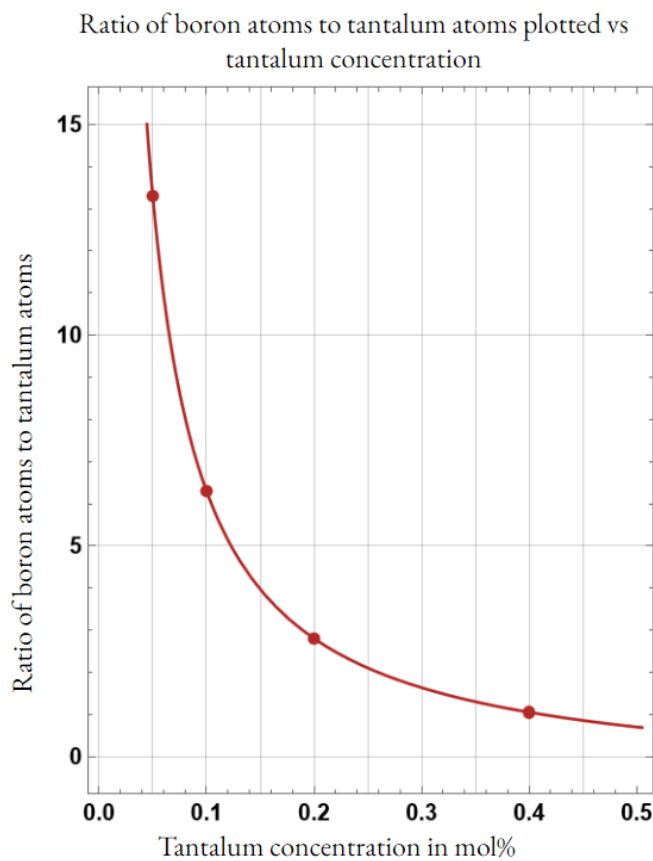


Figure 4. Ratio of boron atoms to tantalum atoms plotted against the concentration of tantalum in mol% for a tantalum lead borate glass described by equation 1 with an $x = 0.3$ and $z = 0$. The dots are at $x = 0.05, 0.1, 0.2$, and 0.4 , corresponding to the four glasses compared in figure 3.

As is apparent, when the tantalum concentration is 5 mol%, there are 13.3 atoms of boron for every tantalum. This means that the tantalum can be well-incorporated into the glass and there should be few regions of pure tantalum, and this is reflected in the data. At 5 mol%, the pure tantalum oxide peaks are fairly small, while the tantalum-boron peaks (particularly TaB_2O_6) are quite substantial. However, if the concentration is increased by just 5 mol%, suddenly that ratio drops by 52.6% to 6.3. This is significant, as this value is similar both to the increase in tantalum oxide and decrease in tantalum boron peaks.

At 40 mol%, the ratio is now 1.05. Because tantalum typically has an oxidation number of 5, this means that at 40 mol%, even if the tantalum were to bond to all of the boron atoms, each atom would have, on average, room for around 4 more electrons. The only possible end result of this is that there are regions of the sample that are just tantalum, resulting in phase separation. And indeed, there was significant visible phase separation at 40 mol% tantalum oxide. It was determined that the sample was phase separated and not crystallized based on the fact that instead of instantly snapping when pressure was applied, it instead bent quite a bit before breaking. Additionally, the coloration and visual structure of the sample were not geometric in nature (like a crystal would be), but instead were streaky and inconsistent.

One thing that is surprising is the B_3O_5 peak. While it does decrease as the tantalum concentration increases, it does not do so at the same startling rate. For example, the difference between the 5 mol% and 10 mol% samples is only a 3.1% decrease (from 33.056 to 32.035). Even

at 40 mol%, the intensity was still at 22.899, only a 30.7% decrease. This would seem to suggest that, while on the whole the sample is becoming dominated by tantalum-rich areas, there are still pockets of lead borate glass. This is one area which further research is required in order to fully understand.

IV. Conclusion

LITOF-MS allows insight into the composition of different glass structures, in particular the medium-range periodic atomic structure of the glass. In this particular application on tantalum lead borate glasses, it has proved quite illuminating. First, the data revealed that the boroxol ring usually present in borate glasses is absent in the tantalum lead borate. While there is a possible explanation for this phenomenon presented in this paper, further research is required in order to fully understand this issue. Additionally, the data regarding tantalum oxide and tantalum-boron compounds correspond quite nicely with theoretical calculations regarding the ratio of tantalum to boron atoms within the glass structure. However, the one exception to this is the B_3O_5 compound, which while still decreasing, does not follow the same pattern as the tantalum-boron compounds, suggesting that even at high concentrations of tantalum there are still regions of lead borate glass. Further research is required to gain a better understanding of this phenomenon.

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