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Journal of Non-Crystalline Solids 293–295 (2001) 416–421

JOURNAL OF
NON-CRYSTALLINE SOLIDS

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Analysis of the structure of lead borosilicate glasses using laser ionization time of flight mass spectroscopy

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Abstract

We report on high resolution laser ionization time-of-flight mass spectroscopy (LITOF-MS) measurements of lead borosilicate and sodium-doped lead borosilicate glasses. This technique permits the observation of intermediate range mesounits, and provides new insights into the glass network structure. In lead borosilicates we observed strong mixing of borate and silicate groupings, a likely absence of diborate units, and the formation of boroxol rings with one lead cation (PbB_3O_6) at borate-rich compositions. The spectra also suggest the growth of a limited lead oxide subnetwork at high Pb contents. In the sodium-doped glasses we see a preference of the sodium for boron units, and the simultaneous appearance of sodium-containing silicate units between 10 and 24 mol% Na_2O , though borate association remains predominant. The reedmergnerite unit ($\text{BSi}_4\text{O}_{10}$) is seen in very small amounts in both glass families. © 2001 Published by Elsevier Science B.V.

1. Introduction

The intermediate structure of glasses remains an important question in the field of glass science. Though new approaches have been tried in the past decade, and advances have indeed been made using neutron scattering, Raman and infrared spectroscopy, and new nuclear magnetic resonance (NMR) methods, no single technique has been able to provide a consistent look at glass networks over this intermediate spatial scale. In this paper we report on our work on this important problem using a new approach, laser photoionization time of flight mass spectroscopy (LITOF-MS). With it we have been able to desorb intermediate range units (mesounits) from the network, and determine their mass and atomic identity precisely. Laser

induced desorption is defined[1] as particle ejection without either surface damage (none observed), and without any significant gas dynamic effects in the plume of particles leaving the surface.

This study will concentrate on heavy metal oxide glasses which have good optical absorption at the laser wavelength. More specifically, we report on our work in glass families $\text{PbO} \cdot \text{B}_2\text{O}_3 \cdot \text{SiO}_2$ and $\text{Na}_2\text{O} \cdot \text{PbO} \cdot \text{B}_2\text{O}_3 \cdot \text{SiO}_2$. These glass families are of importance in traditional glassmaking, and are candidates for a host of optical and detector applications. They also provide a good testing ground for this new technique.

2. Experimental procedures

2.1. Sample preparation

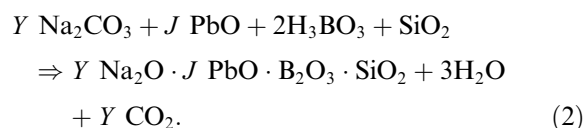
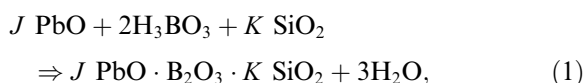
The samples were prepared from high purity (>99.999%) lead oxide, boric acid, silicon dioxide,

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and sodium carbonate. All compounds were thoroughly mixed in platinum crucibles and heated in an electric muffle furnace at 1000 °C. Weight loss measurements were made to ensure the stoichiometries of the samples, and the molten glass was cooled using a roller quenching device. This last step generated thin samples of high visual homogeneity, and provided a consistent cooling rate (approximately 10⁵ K/s). The thin nature of the glasses also made them easy to crush and therefore less likely to become contaminated from the mortar.

The compositions were prepared using the stoichiometric notations:



The parameters *J*, *K*, and *Y* denote the molar ratios of lead oxide, silicon dioxide, and sodium oxide to boron oxide, respectively. This notation allows for easy comparison to NMR data, and simplifies mathematical modeling. For the lead borosilicates, we prepared 12 samples with *J* values 1, 2, 4, 6 and *K* values 0.5, 1, 2, in a ‘grid’ format. For the sodium lead borosilicate samples, we report on the compositions 0.33Na₂O · PbO · B₂O₃ · SiO₂ and 1.05Na₂O · 1.3PbO · B₂O₃ · SiO₂. In this latter stoichiometry the lead content was increased to ensure the high optical absorbance of the sample at 337.1 nm. After the manufacture of the samples, glass shards were selected out to be free of any visible imperfections. They were then ground in a thoroughly cleaned mortar and pestle and mounted in powder form on the sample insertion tip. The tip was immediately inserted into the TOF-MS vacuum chamber and kept at pressures below 5 × 10⁻⁷ Torr.

2.2. Laser ionization mass spectroscopy

A sketch of the experimental setup is shown in Fig. 1. The instrument was a Comstock reflectron

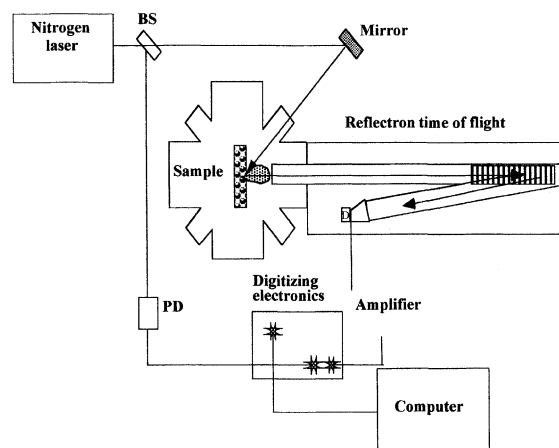


Fig. 1. Sketch of the experimental setup. Some items are not shown, including the camera trained on the sample, ion gauges, etc. BS is the beamsplitter, while PD is the trigger photodiode.

time of flight mass spectrometer with a conical source region and delayed pulse extraction (DPE). The DPE combined with the ion mirror to give consistently high mass resolution, which always exceeded $M/\Delta M = 1500$. The glass units were desorbed using a low power nitrogen laser ($\lambda = 337.1$ nm, <150 $\mu\text{J}/\text{pulse}$ at 10 Hz, 10 ns temporal pulse duration). The glass compositions were chosen to fully absorb all of the laser light at this wavelength. Indeed, the samples were made with lead cations because their optical absorption is due to an electronic transition [2,3] in the outer lead electrons ($^1\text{S}_1 \rightarrow ^3\text{P}_1$), thus concentrating the energy deposition away from the important anionic borate and silicate units, suppressing the likelihood of their fragmentation. A camera was also trained on the sample surface to look for the appearance of plasma or complete powder removal, neither of which was observed in this study.

The spectra were extremely reliable and repeatable, and all data reported consist of an average of 200 spectra each. The samples were rotated during the data acquisition to ensure proper surface sampling. Mass calibration was carried out on a recurrent basis, using a solution of potassium iodide salt dried onto a tip. We estimate the systematic mass error to be no more than 0.2 amu, while the relative error was closer to 0.01 amu. When com-

bined with the peak width, no mass peak was off by more than 0.4 amu. The elemental masses corresponding to the peaks were identified based on their values and on their isotopic abundance signatures, modeled using IsoPro® software. This software does not use or alter the data, but rather illustrates what the mass peak multiplets ought to look like based on their isotopic natural abundance. The results were further confirmed using ^{10}B enriched samples. We did not observe any doubly or more highly charged units, which would have been easily identified from their small isotope separation (e.g., 0.5 vs. 1 amu). We attribute this to the lack of gas phase reactions by the desorbed ions.

Given the novelty of the technique, it is worthwhile to ask whether the observations truly reflect the structure of the glass, or if instead they might represent molecular clusters created in gas phase reactions after the laser desorption. Evidence against this latter possibility is strong, and includes: (a) the peaks in the mass spectra show no laser power dependence (changes in their relative intensities), as would be expected if laser-driven kinetics were responsible for their formation; (b) the laser power was extremely low, causing no visible changes (color defects) in the glass powder; (c) no plasma was observed at any time, indicating a low ion density unlikely to yield recombination; (d) the mass resolution remained very high in all spectra, whereas it would have been severely affected by *any* space charge formation had the ion density been high; (e) the results are consistent with those of other techniques, including NMR and Raman spectroscopies.

Limitations of the technique include its inability to distinguish the geometry of the desorbed units, its need for samples that absorb light at the desorption wavelength, and, in the configuration used by the authors, its current incapacity to measure neutral structures.

3. Results

3.1. Lead borosilicates

Fig. 2 shows a typical negative ion time of flight spectra for the sample $1\text{PbO} \cdot \text{B}_2\text{O}_3 \cdot 1\text{SiO}_2$.

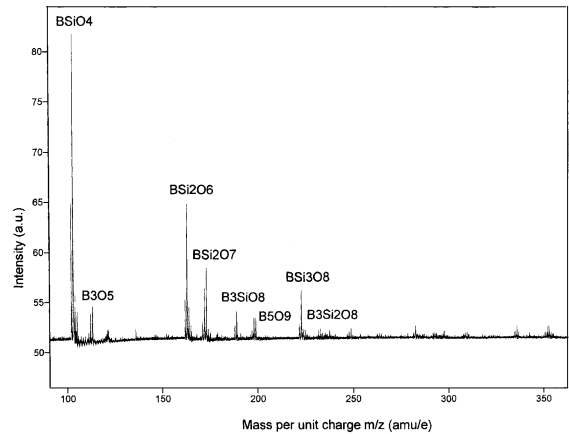


Fig. 2. Negative ion time of flight mass spectrum of the $1\text{PbO} \cdot \text{B}_2\text{O}_3 \cdot 1\text{SiO}_2$ sample. Each peak shows its individual isotopic components. No multiply charged groups are observed.

Note the multiplicity of peaks in each mass group, a consequence of the presence of $^{206,207,208}\text{Pb}$, ^{10}B and ^{11}B natural isotopes. Their natural abundance resulted in unambiguous characteristic patterns which ensured the accuracy of mass assignments.

An important observation is that the negative spectra show a large degree of interaction between borate and silicate units. As the amount of lead oxide in the glasses was increased, the spectra began a clear transition to the same structures we have previously observed [4] in pure binary lead borate glasses (e.g., B_3O_5^- , PbB_3O_6^-). Most of the lead comes out separately in the positive spectra, either as individual ions (Pb^+), clusters of ions (Pb_3^+), or attached to small, stable fragments (PbO^+ , Pb_2BO_3^+ , Pb_3BO_4^+). An example of one such positive spectra is shown in Fig. 3, and it displays the expected Pb^+ ion peak multiplet, smaller amounts of Pb_2^+ as well as the multiple-lead cationic units. Also present is a positive lead oxide unit, Pb_2O^+ , though not in great quantities.

3.2. Sodium-doped lead borosilicates

Fig. 4 illustrates a typical time of flight spectra for the $0.33 \text{Na}_2\text{O} \cdot \text{PbO} \cdot \text{B}_2\text{O}_3 \cdot \text{SiO}_2$ glass in

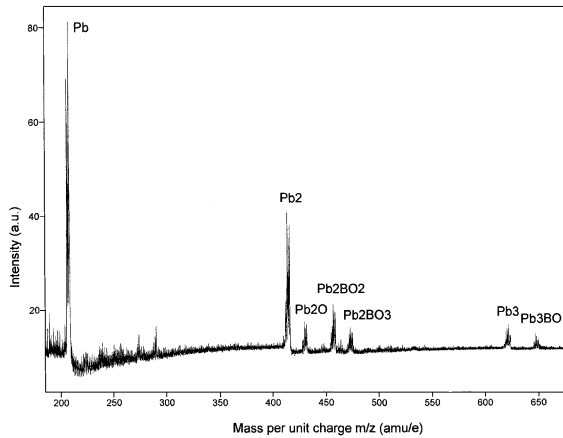


Fig. 3. Positive ion time of flight mass spectrum of the $1\text{PbO} \cdot \text{B}_2\text{O}_3 \cdot 1\text{SiO}_2$ sample. Each peak shows its individual isotopic components. No multiply charged groups are observed.

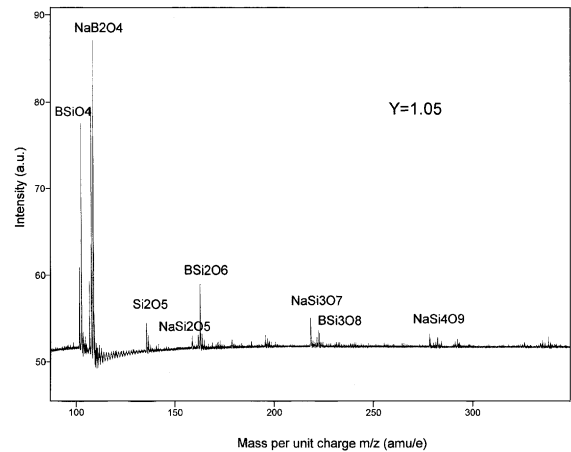


Fig. 5. Negative mode time of flight spectrum of the $1.05\text{Na}_2\text{O} \cdot 1.3\text{PbO} \cdot \text{B}_2\text{O}_3 \cdot \text{SiO}_2$ glass. At this composition all sodium cations go predominantly to borate sites, but silicate units with sodium appear. No multiply charged groups are observed.

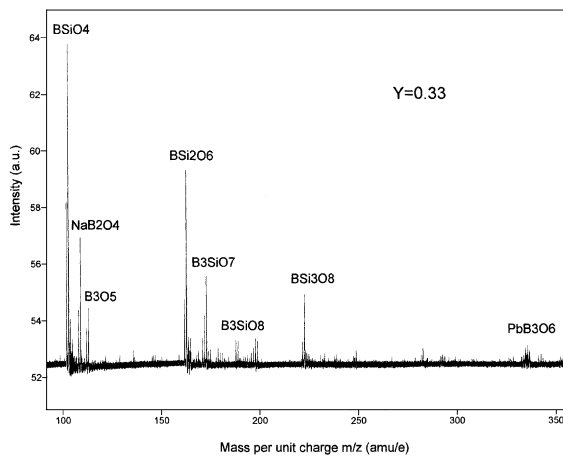


Fig. 4. Negative mode time of flight spectrum of the $0.33\text{Na}_2\text{O} \cdot \text{PbO} \cdot \text{B}_2\text{O}_3 \cdot \text{SiO}_2$ glass. At this composition all sodium cations appear to go to borate sites. No multiply charged groups are observed.

negative ion mode. Many of the desorbed re-ions contained both borate and silicate components. These include BSiO_4 , $\text{BSi}_2(\text{O}_6)$, B_3SiO_7 , B_3SiO_8 and BSi_3O_8 . At this composition the sodium appeared attached only to the borate grouping in the form of NaB_2O_4 . At higher Na contents ($Y = 1.05$) this unit grew quickly, as shown in Fig. 5, and silicate units containing sodium also appeared in smaller amounts.

4. Discussion

4.1. Lead Borosilicates

The negative spectra of the lead borosilicate glasses indicate that the borate and silicate structures in the network interact strongly, coupling with no difficulty. This occurs at all compositions, with the silicate and borate peaks following the expected growth patterns: as we approach the silicate-rich compositions, we see more pure silicate units whereas the borate-rich end reproduces what we have observed [4] in pure lead borate glasses (e.g., $(\text{PbB}_3\text{O}_6, \text{B}_5\text{O}_9)$). For the samples $R = 2$, $K = 0.5$ (silica poor, borate rich) and $R = 2$, $K = 2$ (silica rich, borate poor), compared in Fig. 6, we see an exchange in the height ratio of the BSi_2O_6 and B_3SiO_7 peaks, consistent with the decrease of borons and simultaneous relative increase in silicons. This mixing behavior is also supported by recent NMR work. Wang and Stebbins [5] report that they observe fully random mixing in sodium borosilicate glasses using MQMAS ^{17}O NMR, while Martens and Muller-Warmuth [6] carried out an extensive study of borosilicate and sodium borosilicate samples using ^{11}B , ^{23}Na , and ^{29}Si MAS-NMR. In this latter work the results were

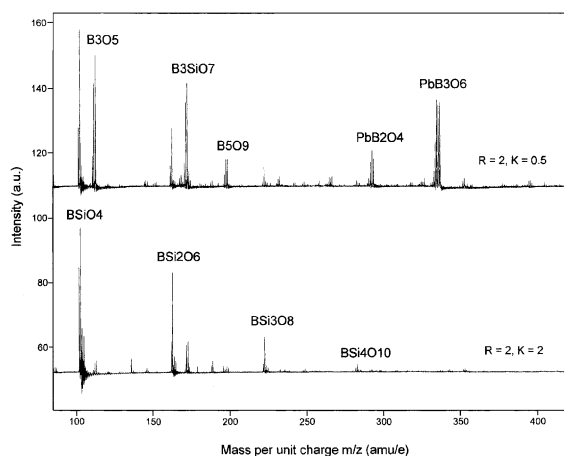


Fig. 6. Comparison of the $R = 2$, $K = 0.5$ (upper) and $R = 2$, $K = 2$ (lower) glass spectra, in negative ion mode.

the same, pointing to a random mixing of boron and silicon polyhedra. These two reports are in disagreement with the earlier work on the sodium borosilicates of Dell et al. [7], where they interpreted their data as indicating little or no mixing, with the possible exception of the proposed reedmergerite ($\text{BSi}_4\text{O}_{10}$) units. For the case of our reported lead borosilicates, the presence of the modifier heavy metal, with its coordination range, makes it more likely that the borate and silicate units would mix strongly.

Looking at the intermediate range mesounits, we see a rapid decline in the amount of PbB_3O_6 units (which we attribute to boroxol or metaborate rings): they have completely disappeared in the sample $R = 2$, $K = 2$, where they were one of the dominant peaks in the low silica sample $R = 2$, $K = 0.5$. We believe that this occurs because of the continuous coupling of the silicate units with the borate ones, which removes the likelihood of formation of mesounits with three borate units. Hence, the decline of pure borate units is accompanied by the formation of B–Si mixed groupings. We also observed a lack of lead cations in many of the borate or silicate units, in either the positive or negative spectra, until high lead contents. The positive spectra do reveal a large peak of single lead cations, suggesting that much of the lead is acting as a relative loose (perhaps interstitial) connection between units.

Worthy of note is the presence, albeit in small amounts, of the $\text{BSi}_4\text{O}_{10}$ reedmergerite group that has long been proposed [7] as a linkage between borate and silicate units. Its observed charge (-1) matches its formal charge, and we see little evidence of fragmentation, thus suggesting that the reedmergerite unit is not the main combinatorial group. Indeed, fragmentation would be confirmed by the presence in the spectra (either positive or negative) of complementary groups which add up to $\text{BSi}_4\text{O}_{10}$, a pattern not seen in our results. No other intact mesounits previously noted in the literature are observed.

In the positive spectra we note the presence of lead (Pb^+ , Pb_2^+) units, as well as oxides (PbO^+). Large clusters of lead oxide are also observed, in small amounts, with masses between 800–1500 amu. This result might be indicative of a growing lead substructure, though the small amounts suggests that this substructure is not dominant, and not enough to consider microphase separation.

4.2. Sodium-doped lead borosilicates

Introduction of sodium cations into the network results in several changes. The sodium appear to prefer borate sites at low modifier contents ($Y = 0.33$), as indicated by the early presence of pure sodium borate NaB_2O_4 units. This changes quickly, however, and by the composition $Y = 1.05$ some of the sodium is being shared with pure silicate (NaSi_2O_5 , NaSi_3O_7 , NaSi_4O_9) units, but the NaB_2O_4 grouping is still dominant. This sharing behavior is also seen in the NMR results [5].

The $Y = 0.33$ sample also shows little indication, in the form of the rather small B_5O_9 peak, of the presence of diborate units, an observation again supported by the NMR measurements of Wang and Stebbins [5]. The spectra also showed a single pure borate structure, namely NaB_2O_4 .

At either composition, the structures containing sodium are always unmixed, i.e. either borate or silicate only. This seems to suggest that the sodium cation goes in preferentially into sites normally occupied by boron atoms in the mixed units. Indeed, all sodium silicate units can be obtained from mixed units by substituting the boron (or silicon) by the sodium and the removal of an ox-

xygen anion, needed for local charge compensation. Thus BSi_3O_8 becomes NaSi_3O_7 , BSi_2O_6 becomes NaSi_2O_5 , and $\text{BSi}_4\text{O}_{10}$ yields NaSi_4O_9 . Even the B_3O_5 unit has its counterpart in the NaB_2O_4 grouping. This might be due to these borate sites having a different local basicity [8,9], making them more attractive to the alkali cations in the melt. This preferential allocation of the sodium to borate sites has been previously noted [10,11] in ^{29}Si MAS-NMR measurements of alkali borosilicate glasses for sodium contents similar to those reported here.

5. Conclusions

We have obtained high resolution time of flight mass spectra of glass structures ablated using laser photoionization. This technique yielded information about the glass network, and is capable of observing mesounits in the intermediate range order. Our main conclusions are:

1. In lead borosilicate glass observations point to a network composed of mixed borate and silicate groupings, coupling with little or no difficulty. At relatively high lead borate contents we recover the binary glass spectra and observe mass peaks we attribute to boroxol (or metaborate) rings.
2. We see little evidence for diborate mesounits, but do observe small amounts of reedmergnerite structures. The number of mesounits in the glasses appear small, suggesting a network made up of smaller, highly interconnected nanounits.
3. There are indication of the formation of lead oxide-rich regions in the lead borosilicates, which may help explain the large glass forming range of this family of glasses.
4. Introducing sodium cations into the a glass network of roughly equal parts of lead, boron, and

silicon oxide results in the formation of NaB_2O_4 units at small sodium contents, and in sodium silicate units at higher Na contents. The sodium borate units remain dominant, however. Sodium cations appear to go in substitutionally for $(\text{BO})^+$.

Acknowledgements

The National Science Foundation is thanked for providing financial support of this research under grant PECASE DMR-9733724. Coe College is thanked for providing summer housing and tuition credit for the students working on this project.

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