



Structure of zinc polyphosphate glasses

B.C. Sales^{a,*}, J.U. Otaigbe^b, G.H. Beall^c, L.A. Boatner^a, J.O. Ramey^a

^a Oak Ridge National Laboratory (ORNL), MS-6056, PO Box 6056, Oak Ridge, TN 37831, USA

^b Department of Materials Science and Engineering, Iowa State University, Ames, IA 50011, USA

^c Science and Technology Group, Corning, Inc., Corning, NY 14831, USA

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Abstract

The technique of high-performance liquid chromatography (HPLC) has been used to determine the distributions of phosphate-anion chains and rings in a variety of zinc-phosphate-based glasses. The phosphate-anion distributions in simple binary zinc phosphate glasses are compared to those found in multi-cation alkali-zinc phosphate glasses. Multi-cation zinc phosphate glasses are chemically durable and can be tailored to exhibit transition temperatures sufficiently low for co-processing with a variety of plastics to form novel organic–inorganic composite materials. The intermediate range order in the multi-cation glasses is found to be similar to that measured in the binary zinc-phosphate glasses. Scanning calorimetry measurements indicate, however, that the multi-cation glasses are more resistant to crystallization than the binary glasses. The fraction of phosphorus sites with 2 (Q^2), 1 (Q^1) and 0 (Q^0) bridging oxygen, as well as the ratio of bridging to non-bridging oxygen (BO/NBO), are obtained from the chromatograms. Structural data for the zinc phosphate glasses obtained using HPLC are compared to results reported in the literature that were deduced using more-traditional solid-state techniques such as NMR, XPS, and Raman spectroscopy. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Zinc phosphate glasses have been investigated for over 50 years [1] and are known to form glasses with unusually high concentrations of zinc oxide, e.g. $[Zn]/[P] \cong 1.2$. The zinc phosphate system has been classified as anomalous [1] (along with the $BeO \cdot P_2O_5$ and $MgO \cdot P_2O_5$ systems) because of an unusual change in various physical properties (e.g. the index of refraction, molar volume, ...) that occurs near the metaphosphate composition:

ZnP_2O_6 . Several workers [1,2] have suggested that one possible origin of this anomalous behavior was an abrupt change in the Zn coordination number at the metaphosphate composition. Recent measurements, however, have shown no significant coordination change at this composition [3–6]. It has also been suggested that Zn acts as a network former in phosphate glasses with a high zinc oxide content. Although the average zinc coordination number is between 4 and 6 in these glasses, high performance liquid chromatography (HPLC) measurements, as discussed below, suggest that even in zinc pyrophosphate glass where $[Zn]/[P]=1$, zinc can be treated as a simple modifier, at least with respect to the dissolution process.

* Corresponding author. Tel.: +1-423 576 7646; fax: +1-423 574 4814; e-mail: vb4@ornl.gov.

Recent interest in the properties of zinc phosphate glasses has been generated by the discovery of Quinn and co-workers [7] of chemically durable alkali-zinc phosphate glasses whose glass transition temperatures are sufficiently low for these substances to be co-processed with a variety of plastics in order to form novel organic-inorganic composite materials. This discovery has sparked a variety of recent investigations of the structure, crystallization behavior, chemical durability, and rheology of zinc phosphate-based glasses [8–13]. In the present article, the technique of high-performance liquid chromatography (HPLC) (this technique is called high-pressure liquid chromatography by some authors) has been used to examine and contrast the distribution of phosphate chains (anions) found in simple binary zinc phosphate glasses with the distributions found in two of the glasses developed by Quinn and co-workers. The HPLC technique provides detailed structural information for phosphate glasses (and crystals) with compositions that fall between the metaphosphate and orthophosphate compositions (these glasses are frequently called polyphosphates). This region encompasses virtually all of the phosphate glasses of current commercial interest.

2. Experimental

The binary zinc-phosphate glasses investigated here were prepared by the reaction of $\text{NH}_4\text{H}_2\text{PO}_4$ with zinc oxide. Appropriate amounts of the reactants were intimately mixed in a ball mill, pre-reacted at 500°C for several hours, melted in a platinum crucible at temperatures of 1100°C for 10–20 h, and then quenched onto a cold copper plate. There was no evidence of reaction between the Pt crucible and the melt. The resulting glasses were clear with very few small bubbles. At each stage of the synthesis, the weight was carefully monitored, and no significant loss of P_2O_5 could be detected. The compositions of the glasses were checked using a combination of energy dispersive X-ray analysis, measured weight loss, and the average chain length as determined from the HPLC chromatograms. As expected from the recent work of Brow and co-workers [8], the batched composition

was virtually identical to final composition of the glass. To obtain the best results from the HPLC measurements, phosphate glasses were prepared with average chain lengths of 2, 4, and 10. The two multi-cation alkali-zinc phosphate glasses were fabricated at Corning and are denoted as Glass A and Glass B. The compositions of these glasses are given in Fig. 3.

The HPLC system and the evidence for the applicability of the HPLC technique have been discussed previously [14–16]. Phosphate glasses and crystals that dissolve faster than about 10^{-11} ($\text{g}/\text{cm}^2 \text{ s}$) at 25°C can be reliably studied using the HPLC method. This includes almost all of the metal-phosphate glasses, in contradiction to ‘conventional wisdom’ [17]. Briefly, the phosphate glasses are partially dissolved in a 0.22 M NaCl and 0.005 M Na_4EDTA aqueous solution which has a pH of 10. The phosphate glasses can be viewed as consisting of chains of corner-linked PO_4 tetrahedra that are bonded to each other via the metal cations. Only the bonds between the metal cations and the non-bridging oxygen are severed during the dissolution process, resulting in the transport of entire phosphate chains into solution. Once the chains are in solution, they are stable against hydrolysis for several days. The longer the phosphate chain, the larger the charge, and the more strongly the chain is bound to the anion exchange column. As the NaCl concentration is increased in the column, the shortest phosphate chains are released first (orthophosphate anion), followed by the next shortest (pyrophosphate anion), etc. The column normally used for phosphate chain analysis can separate chains up to 13 PO_4 tetrahedra in length as well as cyclic phosphate anions such as tri- and tetra-metaphosphate (see Fig. 1). Other columns are available that can separate chains up to 35 PO_4 tetrahedra in length. After the phosphate anions leave the column, they are hydrolyzed to orthophosphate anions in an acidic solution at elevated temperatures and then combined with a molybdenum salt to form a complex ion that absorbs light strongly in the blue. The optical absorption of the effluent stream is measured versus time, and the area under each of the absorption peaks is proportional to the amount of phosphorus in the glass that comes from a

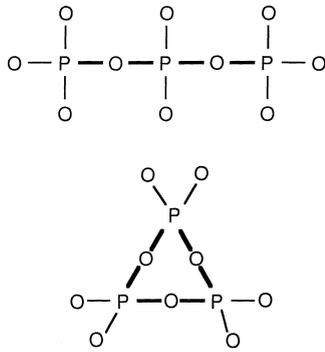


Fig. 1. Schematic illustration of a polyphosphate (P_3) chain anion (top) and a trimetaphosphate (P_{3m}) ring anion (bottom). Bridging oxygen bonds are depicted as thick solid lines, and non-bridging oxygen bonds as thin lines. No phosphorus oxygen double bonds are shown since recent evidence [8] indicates that in polyphosphate glasses, the extra bond is shared equally among all of the non-bridging oxygen. The formal charge of the P_3 anion is -5 and of the P_{3m} anion -3 .

phosphate chain of a particular length. The position of each of the absorption peaks, corresponding to a specific phosphate anion, is calibrated using crystalline phosphate standards. As long as the dissolution of the glass is significantly faster than the rate of direct hydrolysis of P–O–P bonds, this technique provides quantitative information about the distribution of phosphate chains and rings in the glass.

Scanning calorimetry data were obtained using a commercial Perkin–Elmer DSC-4 instrument. Typically, 10–30 mg of glass was measured in a nitrogen atmosphere using a heating rate of $10^\circ\text{C}/\text{min}$. The temperature and the heat flow in the calorimeter were calibrated using a 99.999%-pure indium standard.

3. Results

The chromatograms for the binary zinc phosphate glasses are shown in Fig. 2. The area under each peak, labeled P_n , is proportional to the amount of phosphorus present as a polyphosphate anion consisting of n corner-linked PO_4 tetrahedra with a formal charge of $-(n+2)$, i.e. $(P_n\text{O}_{3n+1})^{-(n+2)}$. In addition to the linear phosphate anions (see Fig. 1), small quantities of the

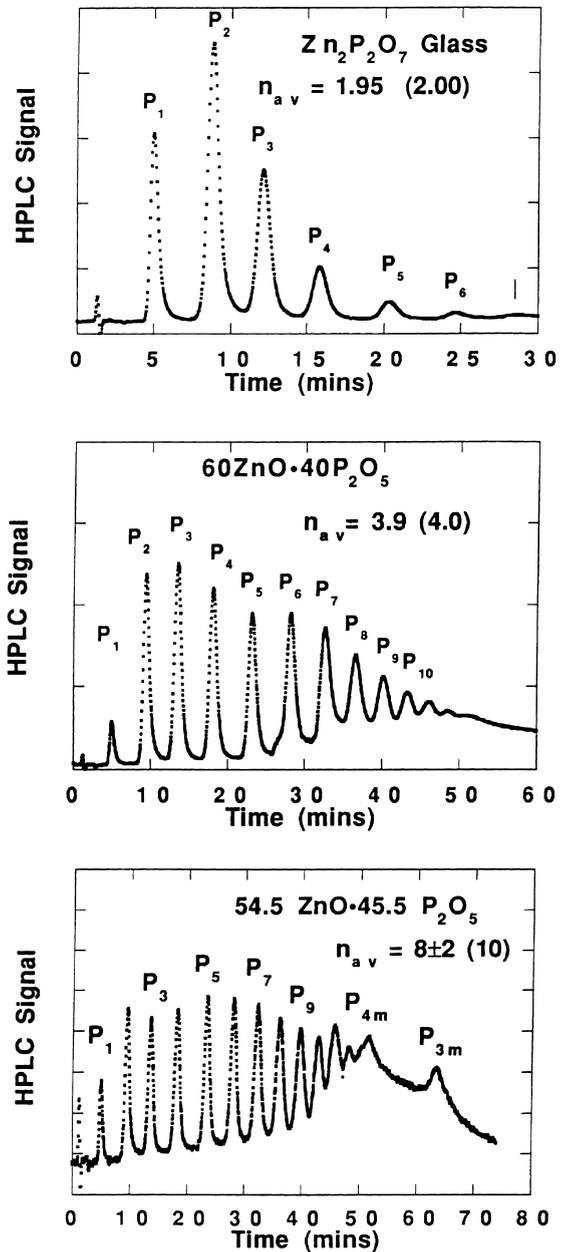


Fig. 2. Chromatograms from binary zinc phosphate glasses. The composition of each glass is given in the figure along with the measured average chain length n_{av} and the value of n_{av} expected from the composition based on Eq. (1) (in parentheses). The area under each peak labeled P_n is proportional to the amount of phosphorus present in the glass in the form of n corner-linked PO_4 tetrahedra [anions of the form $(P_n\text{O}_{3n+1})^{-(n+2)}$]. Cyclic trimetaphosphate (P_{3m}) and tetrametaphosphate anions (P_{4m}) were also detected in the $54.5\text{ZnO}\cdot 45.5\text{P}_2\text{O}_5$ glass.

tetrametaphosphate (P_{4m}) and trimetaphosphate (P_{3m}) ring anions were also detected for the $54.5 \text{ ZnO} \cdot 45.5 \text{ P}_2\text{O}_5$ glass. This glass also had substantial amounts of chains that were too long to be resolved using the present column. These unresolved chains are responsible for the increase in the baseline in the chromatogram of the $54.5 \text{ ZnO} \cdot 45.5 \text{ P}_2\text{O}_5$ glass for times between 45 and 70 min. As expected, the addition of increasing amounts of ZnO results in the formation of shorter polyphosphate chains. The HPLC data from the $60 \text{ ZnO} \cdot 40\text{P}_2\text{O}_5$ glass (Fig. 2) is in good agreement with the paper chromatography data published in 1965 by Meadowcroft and Richardson (MR) [18] on a glass with the same composition. The percentage of phosphorus present in each of the polyphosphate anions agreed to within $\pm 1\%$ with the exception of the phosphorus in the P_6 anion which was reported to be 9% by MR but was found to be 12% in the present experiments. In theory, preparing glasses with different fictive temperatures should effect the distribution of phosphate anions [18]. However, the range of melting temperatures and quench rates commonly encountered in the normal preparation of these glasses was not sufficient to produce any significant variation in the chromatograms.

HPLC data for the two multi-cation alkali-zinc phosphate glasses are shown in Fig. 3 (the as-batched compositions of the glasses are also shown in the figure). The phosphate anion distribution for Glass A (Fig. 3) is quite unusual for a bulk phosphate glass. It is generally very difficult to prepare a binary phosphate glass with an average chain length of 2 or less. (There are exceptions to this statement when one of the metal cations is close to being a glass former like Al^{+3} or Ti^{+4} [19,20] but that is not the case for Glass A shown in Fig. 3.) Glass A has a measured average chain length of 1.69 ± 0.05 while Glass B has a measured average chain length of 2.54 ± 0.05 .

Scanning calorimetry measurements were made on Glass A (alkali-zinc phosphate) and on zinc pyrophosphate glass (Fig. 4). Zinc pyrophosphate glass exhibits a glass transition at about $T_g = 448^\circ\text{C}$ followed by rapid crystallization at $T_{cr} = 550^\circ\text{C}$. The exothermic crystallization corresponds to $\Delta H_{cr} = 1.2 \text{ kcal/mol atoms}$. The thermal

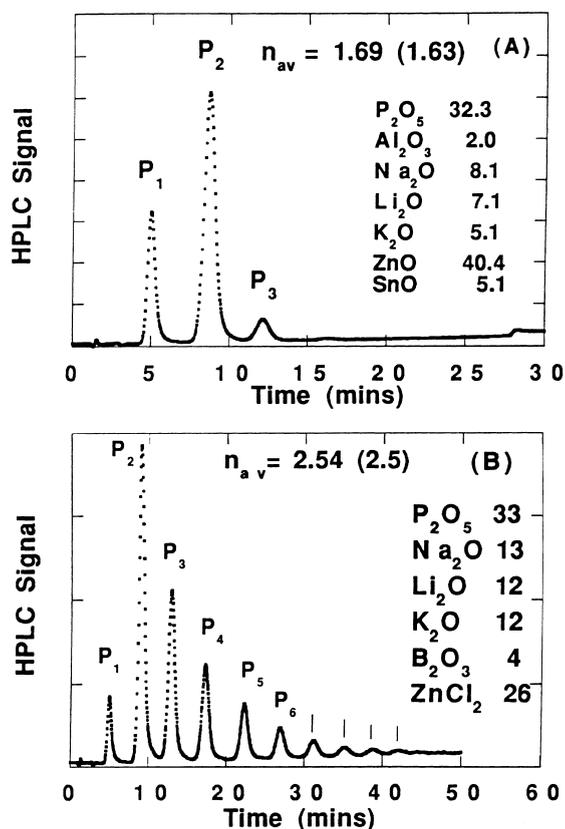


Fig. 3. Chromatograms from two multi-cation glasses fabricated at Corning. The composition of each glass is given in the figure along with the measured average chain length n_{av} and the value of n_{av} expected from the composition based on Eq. (1) (in parentheses). The area under each peak labeled P_n is proportional to the amount of phosphorus present in the glass in the form of n corner-linked PO_4 tetrahedra (anions of the form $(\text{P}_n\text{O}_{3n+1})^{-(n+2)}$).

behavior of zinc pyrophosphate glass is similar to that previously reported for lead pyrophosphate glass [15,21] which had values of $T_g = 390^\circ\text{C}$, $T_{cr} = 430^\circ\text{C}$, and $\Delta H_{cr} = 1.0 \text{ kcal/mol atoms}$, although the smaller temperature difference between T_g and T_{cr} for the lead pyrophosphate glass (40°C) made this glass more difficult to form as bulk pieces. Glass A, however, exhibits a totally different behavior (see Fig. 4). Relative to zinc pyrophosphate, the glass transition temperature is lowered from 448°C to 326°C , and there is no clear evidence of bulk crystallization up to temperatures as high as 600°C . The narrow distribution of

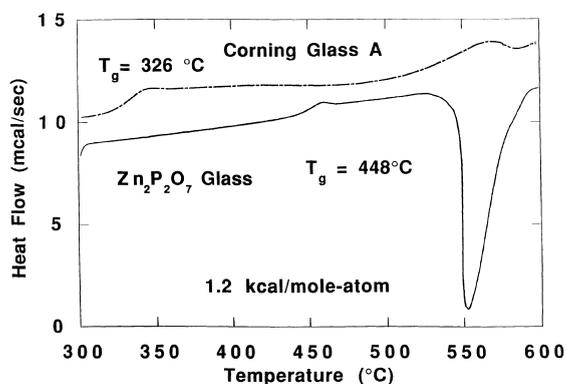


Fig. 4. Scanning calorimetry data for Glass A (top trace) and zinc pyrophosphate glass. The glass transition temperature of each glass is noted in the figure. The heat released during the crystallization of zinc pyrophosphate glass is also shown.

phosphate anions (Fig. 3) should not frustrate the crystallization of this glass, which implies that the large number of different metal cations added to the glass (Zn, Na, K, Li, Al, Ba, and Ca) must prevent the glass from crystallizing easily. The suppression of crystallization through the addition of a large number of different metal cations is well known in the glass industry.

4. Discussion

For a polyphosphate glass (or a glass where small quantities of ring anions can be neglected), the average chain length n_{av} can often be computed directly from the glass composition by equating the charge on the metal cations with the charge on the phosphate chains. For the purpose of computing the total charge contributed by the anions, the glass is envisioned to have only chains of length n_{av} . The total number of phosphate chains is $[P]/n_{av}$ where $[P]$ is the molar concentration of phosphorus in the glass. The charge contributed by these chains is simply the number of chains times their charge or $[P](n_{av} + 2)/n_{av}$. The total charge contributed by the metal cations is $\sum[M_i]q_i$, where $[M_i]$ is the molar concentration of metal i , and q_i is the charge on the metal cation of type i . Equating the charge from the anions and cations gives

$$n_{av} = \frac{2}{\sum_i[M_i]q_i/[P] - 1}. \quad (1)$$

For the binary Zn phosphate glasses with the compositions shown in Fig. 2, this leads to expected average chain lengths of 2, 4, and 10 – in good agreement with the average chain lengths computed directly from the chromatograms (1.95 ± 0.05 , 3.9 ± 0.05 , and 8 ± 2). The large uncertainty in the measured chain length from the $n = 10$ glass is due to the uncertainty in the concentration of chains longer than 13 PO_4 tetrahedra that are not resolved by the column. These chains are responsible for the increase in the baseline for times between 45 and 70 min (Fig. 2). The derivation given above, implicitly assumes that Zn acts as a simple modifier (at least with respect to the dissolution process). Thus, the lack of any significant difference between the expected and measured average chain length lends support to this hypothesis.

For the multi-component alkali-zinc phosphate glasses, the expected average chain length can be calculated from the composition of each glass using Eq. (1) and some simple approximations. For Glass A, all of the metal oxides are treated as modifiers, which leads to an expected average chain length of 1.63, in good agreement with the measured value of 1.69. For Glass B, it is assumed that boron has a charge of 3 and acts as a glass former. With respect to the phosphate anions that are detected using HPLC, as a first approximation, the boron will charge compensate some of the modifying cations which will result in longer phosphate chains. For small amounts of B_2O_3 , this is crudely accounted for by replacing the $[P]$ in Eq. (1) by $[P] + 0.6[B]$. Since there are no unusual peaks in the chromatogram from Glass B, this would suggest that if mixed B and P chain anions are formed in this glass, the B–O–P bonds are broken during the dissolution process. For Glass B, it is further assumed that a large fraction of the Cl (from $ZnCl_2$) is replaced by oxygen during the melting of the glass or during the glass dissolution. The structural role of the remaining Cl in the glass is unclear and was ignored in the application of Eq. (1). With these approximations, the calculated chain length is 2.56, quite close to the measured value of 2.54 ± 0.05 .

The structural data inherent in the chromatograms can be compared to structural data obtained using more-traditional solid-state techniques such as magic-angle-spinning nuclear magnetic resonance (MAS-NMR) and X-ray photoelectron spectroscopy (XPS). In polyphosphate glasses, there are phosphorous ions with 0, 1, or 2 bridging oxygen which are normally called Q^0 , Q^1 and Q^2 sites, respectively. The concentration of these sites in several zinc phosphate glasses was recently reported by Brow et al. [8]. This same information can be easily extracted from chromatograms such as those shown in Fig. 2. The fraction of Q^0 sites is given by the fraction of phosphorus in the P_1 peak. The fraction of Q^1 sites is given by the fraction of phosphorus in the remaining chains that only have one bridging oxygen: $[P_2] + 2/3[P_3] + 2/4[P_4] + 2/5[P_5] + \dots + 2/n[P_n]$. The fraction of Q^2 sites is similarly given by: $1/3 [P_3] + 2/4 [P_4] + 3/5[P_5] + \dots + (n - 2)/n[P_n]$. Phosphorus present in ring metaphosphate anions have only Q^2 sites. A comparison between the HPLC and the NMR data for glasses with the same composition is shown in Table 1. Within the experimental error, the two techniques give identical results.

Oxygen 1s XPS spectra have been used to measure the ratio of the bridging-to-non-bridging oxygen (BO/NBO) in several binary zinc phosphate glasses [9]. This ratio can also be easily extracted directly from the chromatograms. For example, the phosphorus in the P_3 chains, such as shown in Fig. 1, will have two bridging oxygen and eight non-bridging oxygen. In general, a chain of length

n has $n - 1$ bridging oxygen and $2n + 2$ non-bridging oxygen. The ratio of BO/NBO is then obtained by adding up the BO and NBO contributions from each of the peaks in the chromatogram. A comparison between the HPLC and XPS data for zinc phosphate glasses with the same composition is shown in Table 1. Within experimental error, the two techniques give the same results.

An approximate expression for the BO/NBO ratio can be obtained for a polyphosphate glass from the average phosphate chain length n_{av} . If the polyphosphate glass is envisioned as consisting only of chains of length n_{av} , then each chain has $(n_{av} - 1)$ bridging oxygen and $(2n_{av} + 2)$ non-bridging oxygen. Therefore

$$BO/NBO = 0.5(n_{av} - 1)/(n_{av} + 1). \quad (2)$$

This expression should be a good approximation to the BO/NBO ratio. This same expression (in a slightly different form) was used by Gresch et al. [22] and Brow [9] to analyze the XPS data from sodium and zinc phosphate glasses, respectively. Within the scatter of the XPS data, Eq. (2) provided a good fit to all of the XPS data.

Using the same procedures discussed above, the distribution of the Q^i sites and the BO/NBO ratios for the multi-cation alkali-zinc phosphate glasses were extracted from each chromatogram and are given in Table 1. Oxygen XPS data for Glass A was reported by Onyiriuka [23], who found a BO/NBO value of 0.31. This value is substantially larger than the 0.13 value found from the chromatogram. This XPS data, however, was

Table 1

Structural characteristics of Zn phosphate glasses as determined using HPLC, NMR [8], and XPS [9]. The fraction of phosphorus with 2 (Q^2), 1 (Q^1) or 0 (Q^0) bridging oxygen is given, as is the ratio of bridging to non-bridging oxygen (BO/NBO)

Composition	Q^0	Q^1	Q^2	BO/NBO	Techniques
54.5 ZnO	0.0	0.18	0.82	0.4	NMR & XPS
45.5 P ₂ O ₅	0.01	0.15	0.84	0.38	HPLC
60 ZnO	0.0	0.50	0.50	0.30	NMR & XPS
40 P ₂ O ₅	0.02	0.48	0.50	0.28	HPLC
66.7 ZnO	0.13	0.70	0.17	0.10	NMR & XPS
33.3 P ₂ O ₅	0.17	0.65	0.18	0.11	HPLC
Corning (A)	0.23	0.72	0.05	0.13	HPLC
Corning (B)	0.06	0.66	0.28	0.22	HPLC

taken on powder exposed to air which may have been coated with a surface hydroxide layer. The BO/NBO values reported by Onyiriuka [23] for binary zinc phosphate glasses were also much larger than those found by Brow [9] or expected from Eq. (2), lending further evidence to a surface contamination problem in these experiments.

5. Conclusions

High-performance liquid chromatography was used to determine the phosphate-anion chain and ring distributions in a variety of zinc-phosphate-based glasses. The distribution of phosphorus sites (Q^0 , Q^1 , and Q^2) and the ratio of bridging to non-bridging oxygen (BO/NBO) in the glasses were determined from the chromatograms. These data were found to be in good agreement with both MAS-NMR and XPS data obtained for binary zinc phosphate glasses with the same composition. The multi-cation alkali-zinc phosphate glasses had relatively narrow phosphate anion chain distributions. The ease of glass formation in these glasses is attributed to the ability of a large number of different metal cations to frustrate crystallization. All of the HPLC data are consistent with Zn acting as a simple modifier in these glasses.

Acknowledgements

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References

- [1] E. Kordes, W. Vogel, R. Feterowsky, *Z. Electrochem.* 57 (1953) 282.
- [2] E. Kordes, J. Navarette, *Glastech. Ber.* 46 (1973) 113.
- [3] E. Matsubara, Y. Waseda, A. Ashizuka, E. Ishida, *J. Non-Cryst. Solids* 103 (1988) 117.
- [4] E. Matsubara, K. Sugiyama, Y. Waseda, M. Ashizuka, E. Ishida, *J. Mater. Sci.* 9 (1990) 14.
- [5] A. Musinu, G. Piccaluga, G. Pinna, D. Narducci, S. Pizzini, *J. Non-Cryst. Solids* 111 (1989) 221.
- [6] A. Musinu, G. Piccaluga, G. Pinna, G. Valaic, D. Narducci, S. Pizzini, *J. Non-Cryst. Solids* 136 (1991) 198.
- [7] C.J. Quinn, G.H. Beall, J.E. Dickinson, in: *Proc. the 16th Int. Congr. on Glass*, vol. 4, 1992, p. 79.
- [8] R.K. Brow, D.R. Tallant, S.T. Myers, C.C. Phifer, *J. Non-Cryst. Solids* 191 (1995) 45.
- [9] R.K. Brow, *J. Non-Cryst. Solids* 194 (1996) 267.
- [10] U. Hoppe, G. Walter, R. Kranold, D. Stachel, A. Barz, *J. Non-Cryst. Solids* 192&193 (1995) 28.
- [11] R.L. Sammler, J.U. Otaigbe, M.L. Lapham, N.L. Bradley, B.C. Monahan, C.J. Quinn, *J. Rheol.* 40 (1996) 285.
- [12] C.E. Crowder, J.U. Otaigbe, M. Barger, R.L. Sammler et al., *J. Non-Cryst. Solids* 210 (1997) 209.
- [13] J.U. Otaigbe, B.C. Sales, G.H. Beall, *Proc. ACS: Div. Polym. Mat. Sci. Eng.* 76 (1997) 3.
- [14] B.C. Sales, R.S. Ramsey, J.B. Bates, L.A. Boatner, *J. Non-Cryst. Solids* 87 (1986) 137.
- [15] B.C. Sales, J.O. Ramey, J.C. McCallum, L. A Boatner, *Phys. Rev. Lett.* 62 (1989) 1138.
- [16] B.C. Sales, B.C. Chakoumakos, L.A. Boatner, J.O. Ramey, *J. Non-Cryst. Solids* 159 (1993) 121.
- [17] W. Vogel, *Chemistry of Glass*, American Ceramic Society, Columbus, OH, 1985, p. 125.
- [18] T.R. Meadowcroft, F.D. Richardson, *Trans. Faraday Soc.* 61 (1965) 54.
- [19] T. Hayashi, H. Saito, *Phys. Chem. Glasses* 20 (1979) 108.
- [20] R.K. Brow, R.J. Kirtpatrick, G.L. Turner, *J. Am. Ceram. Soc.* 76 (1993) 919.
- [21] B.C. Sales, J.O. Ramey, J.C. McCallum, L.A. Boatner, *J. Non-Cryst. Solids* 126 (1990) 179.
- [22] R. Gresch, W. Muller-Warmuth, H. Dutz, *J. Non-Cryst. Solids* 34 (1979) 127.
- [23] E.C. Onyiriuka, *J. Non-Cryst. Solids* 163 (1993) 268.