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Intermediate-range order in simple metal-phosphate glasses: The effect of metal cations on the phosphate-anion distribution

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Abstract

The technique of high-performance liquid chromatography (HPLC) has been used to determine the phosphate-anion distribution in a variety of metal phosphate glasses-including glasses made with the trivalent metal cations: Al, In, Ga, and La. The composition of each glass was chosen so that the average phosphate chain length was between 2 and 4 PO_4 tetrahedra. The widths of the resulting phosphate-anion chain-length distributions were determined directly from an analysis of the HPLC chromatograms. Literature values for the free energy of formation of the crystalline metal-orthophosphate compounds with respect to P_2O_5 and the metal oxide were compared to the width of the phosphate-anion chain-length distributions. We found that the smaller the energy of formation, the wider the distribution of phosphate chains, and the greater the ease of glass formation. © 1998 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

A variety of metal oxides are frequently added to 'simple' glass forming oxides such as SiO_2, P_2O_5, B_2O_3 or GeO_2 to make the properties of the resulting glass suitable for a particular application. It is well established that the addition of certain metal oxides greatly hinders glass formation while others have a minimal effect. In a simple binary oxide glass (e.g. Na_2O–SiO_2), where only one type of metal cation has been added, the question arises as to what, in fact, determines how a particular metal cation will effect the ease of glass formation. This question has been addressed by several proposed empirical rules that relate the ease of glass formation to the metal-cation's ionic size, field strength, net charge, and electronegativity. One of the more interesting concepts was proposed by Meadowcroft and Richardson (MR) in 1965 [1]. For several monovalent and divalent phosphate glasses, by using solution calorimetry and chromatographic techniques, they showed that the ease of glass formation could be related to the heat of formation of the solid glass (or crystal) with respect to P_2O_5 and the metal oxide. The smaller the heat of formation, the wider the distribution of phosphate chains, and the greater the ease of glass formation.

In glass technology today, the parameter that is most commonly used to classify metal cations is Dietzel's [2,3] field strength. This parameter measures the electrostatic energy between the metal cations and the neighboring oxygen anions. Field strength is particularly useful in parameterizing the physical properties of a multicomponent glass. For example, Hayden et al. [4] found that thermal conductivity, thermal expansion, Young's

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modulus, and the index of refraction systematically varied with the average field strength in complicated multicomponent laser glasses. Although field strength is simple to calculate for a particular glass, the physical relationship between this parameter and the ease of glass formation in a binary metal phosphate glass is not obvious.

The free energy of formation of a crystalline solid provides a measure of the thermodynamic driving force for the creation of a particular compound. For example, if one mole of Na_2O is reacted with two moles of SiO_2, *with respect to the oxides*, the free energy of formation, ΔG, under standard conditions [5,6] is –238 kJ/mol of $Na_2Si_2O_5$. It has been hypothesized since the early days of glass science that smaller free energies of formation implied that glasses made near this composition should exhibit a wider distribution of silicate anions and, hence, should form glasses more easily. This hypothesis is difficult to test in silicate, borate and germanate glasses, because of the inability to obtain reliable information about the distribution of anions in these glasses, and as a result of their tendency to phase separate [7]. Precise information about the distribution of phosphate anions in most metal-phosphate glasses, however, can be determined using high-performance liquid chromatography (HPLC). Phosphate glasses are also less likely to phase separate and thus provide model systems on which to test some fundamental ideas regarding the role of various metal cations in glass formation.

MR [1] showed that the heat of formation (enthalpy) of some binary phosphate crystals and glasses correlated well with the ease of glass formation. Metal phosphate glasses with small heats of formation had broader distributions of phosphate anion chains and, hence, were easier to form as glasses. The purpose of the present work is to test the validity of this idea on a wider range of metal-phosphate glasses. The free energy of formation with respect to the oxides is used to measure the thermodynamic driving force rather than the heat of formation. For solid–solid reactions of the type that characterize the reaction of P_2O_5 with a metal oxide, there is very little difference between these two thermodynamic quantities.

2. Experimental

The metal-phosphate glasses investigated here were prepared by the reaction of $NH_4H_2PO_4$ with the metal oxide or carbonate (metal cations: Li, Na, Ca, Ba, Zn, Pb, Ga, In, Al, La, Y, Sc). Appropriate amounts of the reactants were mixed in a ball mill, reacted at 500°C for several hours, melted in a platinum crucible at temperatures between 800°C and 1450°C for 1–3 h and then quenched onto a cold copper plate. At each stage of the synthesis the weight was measured since glasses that melted at temperatures above 1250°C tended to lose P_2O_5. The compositions of the glasses were measured using energy dispersive X-ray analysis, the measured weight loss, and the average chain length determined from the chromatograms. To obtain the best results from the HPLC measurements, phosphate glasses were prepared with average chain lengths between 2 and 4. The Sc and Y phosphate glasses could not be prepared at temperatures below 1450°C and, hence, were not investigated. What appeared to the eye to be a Ba phosphate glass, in fact, had small crystalline inclusions of $Ba_2P_2O_7$ that were evident in the chromatograms and in the powder X-ray diffraction measurements.

The HPLC experimental system and the applicability of the HPLC technique have been discussed previously [8–10]. Phosphate glasses and crystals that dissolve faster than about 10^{-11} g/cm^2 s at 25°C can be reliably studied using the HPLC technique. This constraint includes almost all metal phosphate glasses. The phosphate glasses to be analyzed are partially dissolved in a 0.22 M NaCl and 0.005 M Na_4 EDTA 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. This severance results 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 an anion exchange column. As the NaCl

concentration is increased in the column, the shortest phosphate chains are initially released (i.e. the orthophosphate anion is released first), followed by the next shortest (i.e. the 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. Other columns are available, however, 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 are 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 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 in the glass.

3. Results

Typical chromatograms are shown in Figs. 1 and 2 for sodium, zinc, aluminum, gallium, indium and lanthanum phosphate glasses. The area under each peak, labeled P_n, is proportional to the amount of phosphorus present as a phosphate anion consisting of n corner-linked PO_4 tetrahedra with a formal charge of $-(n+2)$, i.e., $(P_nO_{3n+1})^{-(n+2)}$. The average phosphate chain lengths, n_{av}, as determined from the chromatograms, were in good agreement with the chain lengths expected from the glass compositions. In addition to the linear phosphate anions (See Fig. 1), for the aluminum phosphate glass a small quantity of the trimetaphosphate ring anion (P_{3m}) was also detected. Trimetaphosphate and tetrametaphosphate ring anions were also present in the lanthanum and indium phosphate glasses (See Fig. 2). In Fig. 1, the distribution of phosphate anions in the sodium phosphate glass is clearly smaller than the distribution from either of the other two phosphate glasses. However, to compare the aluminum and zinc phosphate anion chain-length distributions requires more precision in the analysis of the chromatograms.

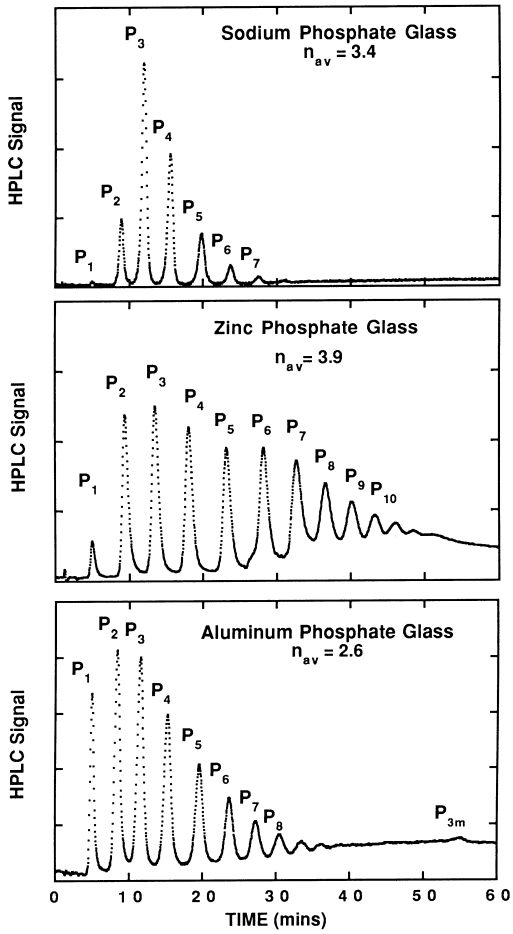

Fig. 1. Chromatograms from metal phosphate glasses made with a monovalent (Na), a divalent (Zn), or a trivalent (Al) metal cation. The compositions of the glasses are $Na_{1.6}PO_{3.3}$, $Zn_{0.75}PO_{3.25}$, and $Al_{0.6}PO_{3.4}$. The area under each peak labeled P_n is proportional to the amount of phosphorus present in the glass in the form of n corner-linked PO_4 tetrahedra (anions of form $(P_nO_{3n+1})^{-(n+2)}$). Cyclic trimetaphosphate anions P_{3m} also were detected in the aluminum phosphate glass.

If the average phosphate chain length is fixed (composition fixed), the largest distribution of

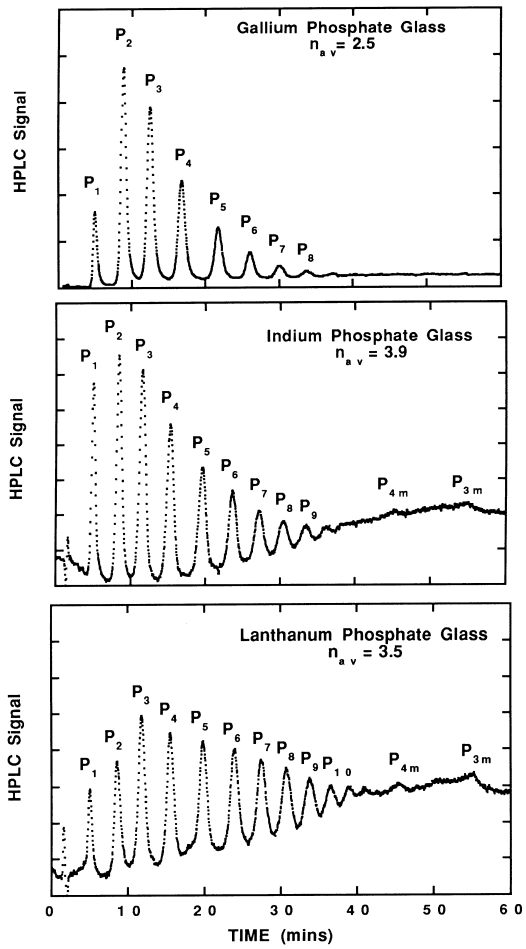

Fig. 2. Chromatograms from metal phosphate glasses made with gallium, indium or lanthanum. The compositions of the glasses are $Ga_{0.6}PO_{3.4}$, $In_{0.5}PO_{3.25}$, and $La_{0.52}PO_{3.28}$. The area under each peak labeled P_n is proportional to the amount of phosphorus present in the glass in the form of n corner-linked PO_4 tetrahedra (anions of form $(P_nO_{3n+1})^{-(n+2)}$). Cyclic trimetaphosphate anions P_{3m} and tetrametaphosphate anions P_{4m} also were detected in the indium and lanthanum phosphate glasses.

anions is given by the Flory distribution [11]. In a Flory distribution, reactions of the type:

$$2(P_nO_{3n+1})^{-(n+2)} \iff (P_{n+1}O_{3n+4})^{-(n+3)} + (P_{n-1}O_{3n-2})^{-(n+1)} \quad (1)$$

have equilibrium constants, K_n, equal to 1. Where K_n is given by

$$K_n = [(P_{n+1}O_{3n+4})^{-(n+3)}][(P_{n-1}O_{3n-2})^{-(n+1)}] / [(P_nO_{3n+1})^{-(n+2)}]^2. \quad (2)$$

In disproportionation reactions of the type shown in Eq. (1), charge, the phosphorus concentration, and the oxygen concentration all are preserved. An equilibrium constant of one implies that $\Delta G = 0$ for Eq. (1). All of the phosphate anion distributions are smaller than the Flory distribution primarily because the equilibrium constants, K_n, are less than 1 for $n = 2$, 3 or 4. For longer chains (larger n), $K_n \cong 1$. K_n's less than 1 correspond to endothermic enthalpy changes associated with reaction (1). For a variety of alkali and alkaline earth phosphate glasses, MR found K_n to be independent of the average phosphate chain length. This independence implies that one way of comparing the magnitudes of the phosphate anion distributions from glasses with different average chain lengths, is to compare K_ns. As n is increased, K_n should approach 1 more quickly in metal phosphate glasses that form easily.

4. Discussion

Fig. 3 shows the values of K_2, K_3, and K_4 obtained from the chromatograms of various metal phosphate glasses. The ordering of the cations on the abscissa is in accordance with the free energy of formation of the crystalline orthophosphates with respect to the oxides (See Fig. 4). Na_3PO_4 has the largest free energy of formation, and $AlPO_4$ the smallest. No free energy data could be found for $InPO_4$, $GaPO_4$, $LaPO_4$, so these cations were placed on the abscissa such that the K_ns formed a smooth curve. The free energy of formation (per mole of atoms) of $GaPO_4$ should be close to that of $Zn_3(PO_4)_2$, and the formation energy for $InPO_4$ and $LaPO_4$ should be similar to that of $AlPO_4$. The magnitude of the phosphate chain-length distributions increases as the metal cation is changed from Na to La- suggesting that metal phosphate glasses with smaller formation energies do, indeed, form glasses more easily as suggested by MR. Although the above analysis only considered the energy of formation of crystalline orthophosphates, MR [1] showed that for the alkali

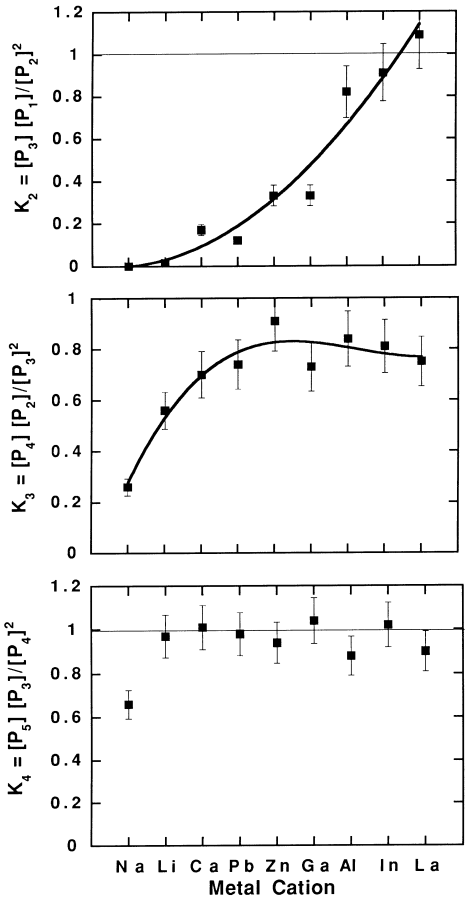

Fig. 3. Equilibrium constants determined from the chromatograms for reactions illustrated in Eq. (1) vs. the metal cation. The ordering of the cations on the abscissa is in accordance with the free energy of formation of the crystalline orthophosphates with respect to the oxides. The lines through the data are guides to the eye.

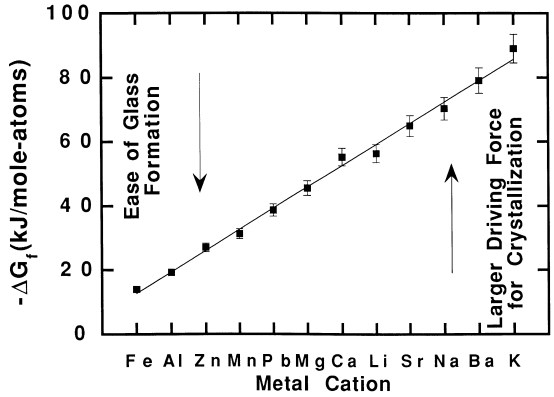

Fig. 4. Free energy of formation of the crystalline orthophosphates with respect to P_2O_5 and the metal oxide. A large energy of formation implies a strong driving force for crystallization and a narrow distribution of phosphate anions in the glass. A small energy of formation facilitates the formation of a glass with a wide distribution of phosphate anion chain lengths. The line through the data is a guide to the eye.

Table 1
Classification of the metal cations in a simple phosphate glass by Dietzel's field strength parameter [3] or by the free energy of formation of the metal orthophosphate [5,6] with respect to the oxides

Cation (field strength) valence (Å^2)	Cation (free energy of formation) (kJ/mol-atoms)
K (0.13)	K (89)
Na (0.19)	Ba (79)
Li (0.23)	Na (70)
Ba (0.26)	Sr (65)
Pb (0.27)	Li (56)
Sr (0.28)	Ca (55)
Ca (0.33)	Mg (45)
Mg (0.45)	Pb (38)
Mn (0.49)	Mn (31)
Zn (0.50)	Ga (30) [a]
La (0.54)	Zn (27)
In (0.67)	Al (19)
Fe (0.76)	La (19) [a]
Ga (0.78)	In (19) [a]
Al (0.84)	Fe (14)

[a] Approximate values for the energy of formation have been estimated for Ga, La, and In orthophosphates using the equilibrium constants shown in Fig. 3.

and alkaline earth phosphate glasses, this conclusion also applied if other crystalline phosphates were considered (such as pyrophosphates).

Finally, it is interesting to compare (Table 1) the classification of metal cations in phosphate glasses using the Dietzel field strength parameter, and the free energy of formation of the orthophosphates. Using Dietzel's classification, all monovalent cations have smaller field strengths than divalent cations which in turn are smaller than all trivalent cations. The metal cation classification scheme using free energy is similar to field strength but the cations are not simply grouped according to charge. In the free energy scheme, the relative ordering within the alkalis (or within the alkaline earths) is the same in both schemes. However,

some alkaline earths, such as Ba or Sr, have larger free energies than the alkali Li. This difference is in agreement with our experimental observation that Ba phosphate glasses were more difficult to prepare than Li phosphate glasses. It would be interesting to investigate what other physical properties (such as Young's modulus or the thermal conductivity) varied systematically with free energy of formation values.

5. Conclusions

The distributions of phosphate anion chain lengths were measured for a variety of metal-phosphate glasses using the technique of HPLC. From each chromatogram, equilibrium constants, K_n, (See Eq. (2)) were calculated for the metal phosphate glass. For a given metal phosphate glass, the more rapidly K_n approached 1 with increasing n, the greater the distribution of phosphate anion chain lengths, and the greater the ease of glass formation. The ease of glass formation correlated well with the literature values for the free energy of formation of the crystalline orthophosphates as measured with respect to P_2O_5 and the metal oxide. The ease of glass formation did not correlate as well with the metal-oxygen field strength.

Acknowledgements

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References

[1] T.R. Meadowcroft, F.D. Richardson, Trans. Faraday Soc. 61 (1965) 54.
[2] A.Z. Dietzel, Electrochem. 48 (1942) 9.
[3] W. Vogel, Chemistry of Glass, American Ceramic Society, Columbus, Ohio, 1985, p. 38.
[4] J.S. Hayden, Y.T. Hayden, J.H. Campbell, High Powered Lasers and Applications, SPIE Publications, Bellingham, Washington, 1277, 1990, p. 121.
[5] J.A. Dean, Lange's Handbook of Chemistry, McGraw Hill, New York, 1992, Sections 4.5 and 6.1.
[6] J.R. Van Wazer, Phosphorus and its Compounds: Chemistry, Interscience, New York, vol. 1, 1980, p. 889.
[7] W. Vogel, Chemistry of Glass, American Ceramic Society, Columbus, Ohio, 1985, p. 125.
[8] B.C. Sales, R.S. Ramsey, J.B. Bates, L.A. Boatner, J. Non-Cryst. Solids 87 (1986) 137.
[9] B.C. Sales, J.O. Ramey, J.C. McCallum, L.A. Boatner, Phys. Rev. Lett. 62 (1989) 1138.
[10] B.C. Sales, B.C. Chakoumalos, L.A. Boatner, J.O. Ramey, J. Non-Cryst. Solids 159 (1993) 121.
[11] J. Flory, Am. Chem. Soc. 64 (1942) 2205.