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Statistical approach to modeling relationships of composition – structure – property I: Alkaline earth phosphate glasses

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This paper introduces a methodology of accurate property predictions for amorphous materials (focusing on oxide phosphate glass) based on statistical composition (C) – structure (S) – property (P) modeling. Utilizing literature reported ^{31}P MAS NMR data (Q^n, δ_{iso}, η) of binary alkaline earth phosphate glasses RO-P_2O_5 (R = Mg, Ca, Sr, Ba), unified relationships of RO and Q^n ($n = 2, 3$) were firstly established. A statistical approach to modeling mathematic relationships of C-S, S-P and then C-S-P for the alkaline earth binary phosphate glasses was illustrated step by step. The C-S models of Q^2 and Q^3 were then used to calculate Q^2 and Q^3 in the mixed alkaline earth (MAE) phosphate glass, MgO-CaO-P_2O_5, which in turn result in S-P models accurately tracks the glass properties, density, Young's modulus, glass transition temperature, and Microhardness. The S-P models were also used to simulate non-linear relationships of the MAE phosphate glasses as a function of $Q^2/(Q^2+Q^3)$ from the glass network structure view point in comparison with the property responses to the change of MgO/(MgO + CaO). Within the entire composition space of the alkaline earth phosphate glasses with $RO/P_2O_5 \leq 1$, the statistical C-S-P modeling for predicting glass properties, including glass transition temperature, Young's modulus, density, etc., requires no assumptions on glass structures or other constraints as compared with other theoretically based modeling approaches.

1. Introduction

Phosphate glasses, including rare earth containing phosphate glasses, have found a variety of specialty applications in optical communications [1], optical switching devices [2], lasers [3], three-dimensional displays [4], electronic sealing [5,6], and immobilization of nuclear waste materials [7,8], etc. Furthermore, phosphate glasses of different chemistries show vast different chemical resistance to corrosion in aqueous solutions by as much as several orders of magnitudes. Depending on specific applications, the composition can be designed/adjusted [9,10]. Over several decades significant progress has been made in glass structure characterization and modeling, including Raman [11] and FTIR [12] spectroscopy, X-ray photoelectron spectroscopy (XPS) [13], extended X-ray absorption fine structure (EXAFS) [14], neutron diffraction analyses [15], and solid state, magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy [16], which provided detailed, complementary information on local chemical environments of the glasses [17,18]. NMR is one of the spectroscopic tools under a rapid development, which has been routinely used to quantitatively probe glass for composition, temperature, and pressure related local structural changes over the intermediate range and the connectivity of the glass network (silicate, borate, phosphate, etc.) with specific metal cations of interest, as well as hydroxyl groups [19].

Statistical modeling approach to glass composition and property relationships has been widely used in research and industry in general, for example, its application in modeling nuclear waste glass chemical durability and the related melting properties, which is the most complex glass system of alkali-aluminoborosilicate glasses, containing more than 30 glass constituents [20,21]. Recently statistically derived glass structure models have been constructed to predict properties of phosphate glasses [22], in which non-linear response of the glass properties to composition change were reasonably correlated with a linear combination of

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key glass network structure units, deduced from the FTIR or Raman spectra based on linear statistical least square regression analysis. In another words, glass properties can be predicted by linear statistical models established from the composition and structure information, which constitutes the methodology of composition (C) - structure (S) - property (P) statistical modeling. In our present study, the previously proposed statistical method was further demonstrated by using a set of structure information derived from a much more accurate structural testing method – MAS NMR, illustrating how the statistical C-S-P tool can be used for research and composition design in material science.

^{31}P MAS NMR studies of alkaline earth binary phosphate glasses as a part of our ongoing C-S-P modeling work, focusing on phosphate glasses. Composition affects glass property by changing the network structures, i.e., the distribution Q^n (Q represents a PO_4 tetrahedral unit, n represents the number of bridging oxygen per PO_4 unit, $n = 0, 1, 2, 3$). The Q^n groups can be accurately detected by using MAS NMR technique, which enables us to build statistical relationships among composition, structure, and property. In Part 1 of the series, as reported here, statistical modeling based on the ^{31}P MAS NMR results (Q^n, δ_{iso}, η data) of alkaline earth phosphate glasses $RO - P_2O_5$ (R = Mg, Ca, Sr, and Ba) in literature will be detailed [23–25]. In Part 2, we plan to expand the C-S-P modeling to $M^I_2O - P_2O_5$ and $M^{II}_2O - P_2O_5$ where M^I and M^{II} represents monovalent alkali cations (Li, Na, K, Cs) and divalent cations (Zn, Mn, etc.). In Part 3, ternary phosphate systems containing Al_2O_3, B_2O_3, SiO_2, GeO_2, etc., will cover statistically modeling structure units of $^{[4,5,6]}$Al, $^{[3,4]}$B, and $^{[4,5,6]}$Si (left superscript represents coordination of a given cation with oxygen) determined by ^{27}Al, ^{11}B, and ^{29}Si MAS NMR measurements in addition to Q^n.

Statistical mixture composition modeling, or C-P modeling, has been widely utilized to aid glass design for target properties and related glass melting process control [26,27]. It is fair to say that glass structures key to these properties have been missing from the C-P modeling approach in reality. There is a growing number of studies using glass topological approach to model glass properties [28–30], for which several assumptions on the glass network structures are required based on the corresponding glass compositions. The related structure units can be theoretically calculated based on glass composition with the absence of spectroscopic fingerprints of the glass network structures. The approach can be also categorized as the C-S-P modeling. As will be detailed in this paper, the statistically based C-S-P modeling combines the well-established methodology of linear statistical regression analysis with spectroscopically determined fingerprints of the actual glass network structures of known glass compositions and properties to aid future glass design and process control in principle.

2. Relations of Qn and O/P ratio in binary alkaline earth phosphate glass

The network of phosphate glass is basically composed of various structure units with different degree of linkages of Q^n (n = 0–3) groups, as illustrated in Fig. 1. Specifically, ultraphosphate glass (P_2O_5) with O/P of 2.5 contains 100% Q^3 groups, which has three P-O-P bridging oxygen bonds (*BO*) and one P=O double oxygen bond (*DOB*). Each tetrahedron unit is connected with three units at the corners, forming three-dimensional network. Metaphosphate glass ($M^I_2O \cdot P_2O_5$, $M^{II}O \cdot P_2O_5$ or $M^{III}_2O_3 \cdot P_2O_5$ where M^I, M^{II} and M^{III} are the mono-,bi- and tri-valence cation, respectively) with O/P of 3.0 contains 100% Q^2 units (PO_3^-); the structure unit has two *BO*s, the other two non-bridging oxygen ($P-O^-$) bonds (*NBO*) share the negative charge and *DOB* [31]. One tetrahedron unit is connected with two tetrahedral units at the corners, forming two-dimensional chain network. Pyrophosphate glasses ($2R^I_2O \cdot P_2O_5$ or $2R^{II}O \cdot P_2O_5$) with O/P of 3.5 contain only one *BO*, which is Q^1 ($P_2O_7^{4-}$) units [31,32]. One tetrahedron unit is generally connected at the end of phosphate chain or in the form of dimers with another tetrahedral unit. Orthophosphate glasses ($3M^I_2O \cdot P_2O_5$, $3M^{II}O \cdot P_2O_5$ or $3M^{III}_2O_3 \cdot P_2O_5$) with O/P of 4.0 contain Q^0 (PO_4^{3-}) units, and each unit has four *NBO*s [31,32]. Overall, the degree of polymerization of the glass network follows the rank $Q^3 > Q^2 > Q^1 > Q^0$, the mixture of which dictates the glass properties.

The distributions of Q^n groups in phosphate glass can be determined quantitatively by using ^{31}P MAS NMR spectroscopy, from which isotropic chemical shift, i.e., δ_{ISO}, chemical shift anisotropy ($\Delta\delta$), and asymmetry (η) provide a full set of Q^n structure characterization [19,21,22]. Combining Q^n and these three parameters (δ_{ISO}, $\Delta\delta$, η), effect of glass composition on both Q^n and its related local environment can be further examined.

Fig. 2 depicts Q^n and δ_{ISO} as a function of RO/P_2O_5 for binary alkaline earth phosphate glasses [19,23,24], which shows coexistence of Q^3 and Q^2 determined by ^{31}P MAS NMR measurements. For a majority of the glasses, Q^1 groups were well below 8%, except for two glasses with the highest MgO (54 and 59 mol%), which have 18% Q^1 and 44% Q^1, respectively, and zero Q^3. Clearly shown are the unified Q^n relationships that Q^2 increases linearly, from 0 to 100%, as RO/P_2O_5 increases from 0 to 1 (or O/P from 2.5 to 3.0), independent of the type of alkaline earth cation or its ionic potential (defined by formal charge of cation divided by (effective radius of cation)^2). The opposite trend holds for Q^3, which decreases from 100% to 0 as RO/P_2O_5 increases from 0 to 1. For RO/P_2O_5 between 1 and 2 (O/P from 3 to 3.5), projections from the limited data ($MgO-P_2O_5$ system) suggest that Q^2 decreases from 100% to 0, while Q^3 ceases to exist and Q^1 increases from 0 to possibly 100% (cf. the dash line in Fig. 2).

The speciation reaction of phosphate groups in the above cited binary phosphate glasses can be described by the reaction, $2Q^3 + RO \rightarrow 2Q^2$ ($RO/P_2O_5 < 1$ or $O/P < 3.0$), in general where Q^1 does not exist or negligibly small [33,34]. When RO/P_2O_5 becomes greater than 1, the speciation of $2Q^2 + RO \rightarrow 2Q^1$ ($RO/P_2O_5 > 1$ or $O/P > 3.0$) proceed with zero or negligible Q^3. Similar speciation reactions in binary alkali phosphate glasses have been proposed by Brow et al. [33].

Over the RO/P_2O_5 range from the current survey (cf. Fig. 2), δ_{ISO} ratios are grouped according to the type of alkaline earth oxides, which is affected by the electron density (or electron shielding), bond angle, and local structure asymmetry surrounding the phosphorous [23,35]. In general, δ_{ISO} becomes more negative for less shielded P nucleus as cationic potential (charge/radius) increases for the metal oxides, implying increase in M-O covalency, depleting electron density on the phosphorus. For Q^2 units, the $MgO-P_2O_5$ glasses have the lowest δ_{ISO} ratios, while the highest ratios belong to the $BaO-P_2O_5$ glasses. Both $CaO-P_2O_5$ and $SrO-P_2O_5$ glasses show almost the same trend of δ_{ISO} - RO/P_2O_5. In addition, δ_{ISO} appears to increase linearly with RO/P_2O_5, which is mostly sensitive to the concentration change of CaO/P_2O_5 and SrO/P_2O_5, but the least sensitive to the change of MgO/P_2O_5. The same parallel trends also hold for Q^3 groups, except that δ_{ISO} appears to be independent of MgO/P_2O_5.

Based on the above analysis, the unified relationships of Q^2 - RO/P_2O_5 and Q^3 - RO/P_2O_5 suggest that averaged phosphate structures of Q^2 and Q^3 created by RO modifications to the network are independent of the specific RO type, at least when RO is less than P_2O_5. However, averaged bond strength and structural asymmetry of Q^n units, as characterized by δ_{ISO} and η (not shown for a lack of complete data set from the literature) [19,23,24,31–34] have noticeable variations depending on ionic strength of the alkaline earth cations.