

**[phosphate glasses] Structural variation in phosphate glasses by metal-oxide modifying cations** supplementary to {§14.3:460}

In glassy and crystallite phosphates the basic building blocks are  $\text{PO}_4$  tetrahedra, of which  $s^3p$  hybridization of the P outer electronic orbitals ( $3s^2)(3p^3$ ) gives rise to the directional  $\sigma$  – bonding between the P and O atoms. The remaining electron of P is promoted to the  $3d$  orbital, resulting in a  $d\pi - p\pi$  bonding between P and O. In pure  $\text{P}_2\text{O}_5$  the  $\text{PO}_4$  tetrahedra are connected by sharing up to three oxygen atoms (bridging O) to form a three-dimensional (3D) network. However, the nonbridging O is associated with the  $\text{P}=\text{O}$  double bond whose  $\pi$ -character is energetically unbalanced and unstable, opposing the cross-linking network. Pure glassy and crystalline  $\text{P}_2\text{O}_5$  are extremely hygroscopic and volatile. Incorporating counter cations, i.e., network modifiers such as H, alkali, alkali-earth or transition metals, to create additional nonbridging O quickly improves the stability. Accordingly, introducing metal oxides into  $\text{P}_2\text{O}_5$  will generate additional nonbridging O-M-O linkages across different  $\text{PO}_4$ -chains thereby forming a more stable structure. In the case of oxides of divalent metals such as  $\text{PbO}$ , in principle, all the  $\text{P}=\text{O}$  bonds are replaced by  $\text{P}-\text{O}-\text{M}$  at 33 mol% of metal ions. The 3-D network transforms into a complex  $\text{PO}_4$ -chain-like structure in which the average number of  $\text{PO}_4$  units per chain varies from infinity (*metaphosphate*) at 50 mol% to 2 (*pyrophosphate*) at 66.7 mol% MO concentration. Figure 1 depicts a 2-D schematic representation of these structural changes in phosphate glasses by monovalent metal oxide ions,  $\text{M}_2\text{O}$ . This is a rudimentary and qualitative description of the structural modification process. Neutron-diffraction studies are useful in gaining insights into atomic correlations between the modifier and the  $\text{PO}_4$  ions in phosphate glasses.

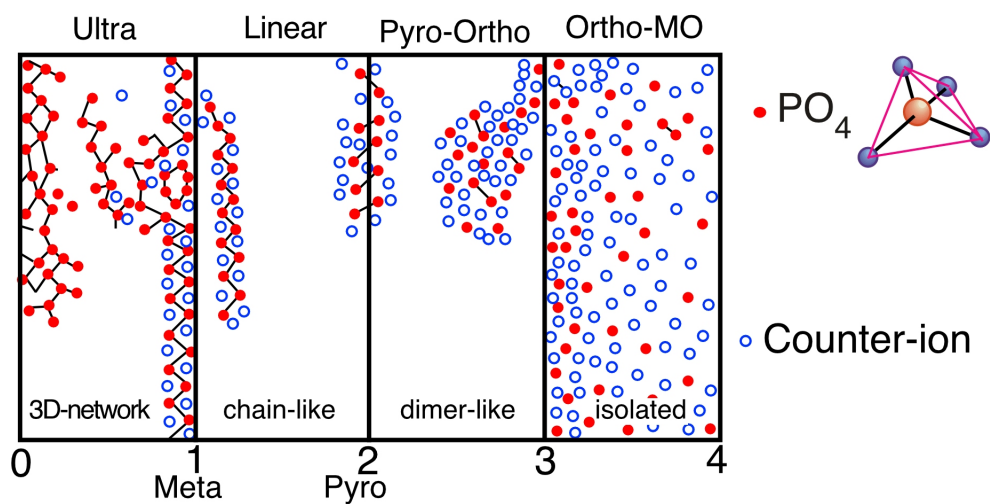


Figure 1 A simplified 2-D representation showing a schematic of the structural transformation of phosphate glasses modified by counter ions. [After Van Wazer (1958)].

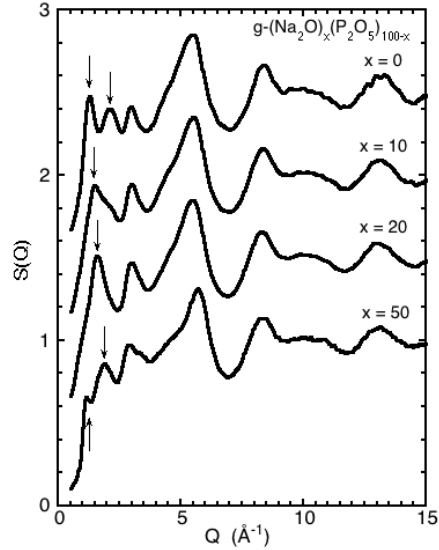


Figure 2 The neutron structure factors of  $(\text{Na}_2\text{O})_x(\text{P}_2\text{O}_5)_{100-x}$  glasses. Successive curves are shifted upward by 0.5 for clarity. [After Suzuya, Price, et al. (1998)]

Figure 2 shows the static structure factors of glassy  $(\text{Na}_2\text{O})_x(\text{P}_2\text{O}_5)_{100-x}$  ( $x = 0, 10, 20,$  and  $50$ ). With increasing  $\text{Na}_2\text{O}$  modifier contents, we expect the breakup of the 3-D network of  $\text{PO}_4$  units in pure  $\text{P}_2\text{O}_5$  to  $\text{M}_2\text{O}$ -intercepted  $\text{PO}_4$  chains and eventually to dimers and individual ions. In diffraction studies this breakup of the 3D  $\text{PO}_4$  network will manifest itself in the intermediate-range-order (IRO) and extended-range-order (ERO) structures. In phosphates, the approximate characteristic correlation lengths for SRO, IRO, and ERO are  $r < 2.5\text{\AA}$ ,  $2.5 < r < 5\text{\AA}$ , and  $r > 5\text{\AA}$ , respectively. This implies changes corresponding to IRO and ERO will appear mainly in the low  $Q$  region ( $< \sim 3\text{\AA}^{-1}$ ). For  $x=0$  (pure  $\text{P}_2\text{O}_5$  glass) the first two peaks at  $1.30$  and  $2.12\text{\AA}^{-1}$  are due to IRO of the P-O network. To understand the structure, the data may be studied in terms of random packing of the structural units, i.e.,  $\text{P}_2\text{O}_5$  species. For example, one may fit the  $g\text{-P}_2\text{O}_5$  data by relaxing the crystalline counterpart,  $c\text{-P}_2\text{O}_5$ —two  $\text{P}_4\text{O}_{10}$  molecules in a pseudo-body-centered unit cell of space group symmetry  $R_3C$ . This leads to a picture of packed, orientation-correlated  $\text{P}_4\text{O}_{10}$  molecule-like units for  $g\text{-P}_2\text{O}_5$ . Next, the IRO structural change is clearly evident from the replacement of the two peaks in  $g\text{-P}_2\text{O}_5$  by a single peak for the 20 mol%  $\text{Na}_2\text{O}$  glass at  $1.60\text{\AA}^{-1}$ , which corresponds to a correlation length of  $3.7\text{\AA}$ . This indicates that the IRO structure characteristic of a  $\text{P}_4\text{O}_{10}$  molecule unit in the  $g\text{-P}_2\text{O}_5$  is broken down into smaller units by the modifier cations. As the composition of  $\text{Na}_2\text{O}$  changes from 20 to 50 mol%, the IRO peak shifts to higher  $Q$ , indicating further destruction of the  $\text{PO}_4$  linkage. Moreover, a new peak arises at  $1.16\text{\AA}^{-1}$  for the 50 mol% composition, suggesting the onset of an ERO of a length scale of  $\sim 5.4\text{\AA}$ , presumably due to the formation of a  $\text{PO}_4$  chain-like structure in the metaphosphate. All these observations of IRO and ERO structural changes are in sharp contrast with the SRO. For  $Q$  beyond  $\sim 3.5\text{\AA}^{-1}$ , the structure factors of all composition are essentially the same. This indicates that addition of the  $\text{Na}^+$  modifier to  $g\text{-P}_2\text{O}_5$  has little effect on the SRO where the basic  $\text{PO}_4$  tetrahedral structure is retained.

These afore-mentioned examples show the challenging task in understanding the nature of IRO and ERO in amorphous materials from experimental data obtained not only in neutron and

x-ray diffraction, but also in other solid-state spectroscopic techniques such as NMR, EXAFS, Mössbauer, EPR, and optical-absorption methods. All of them lack either the sensitivity or contrast to detect the distribution of structural units, e.g., PO<sub>4</sub> corner sharing chain-like species, of the size of about 10-500 Å. *High-performance liquid chromatography* (HPLC) is unique in characterization of intermediate-sized PO<sub>4</sub> chain-like and ring-like species. Because phosphate glasses dissolve in aqueous solutions with an added chelating agent in such a way that the structural units PO<sub>4</sub> remain intact, separates in an analytical column and consequently can be quantified by measuring ultraviolet absorption rates in the reagent stream. Structural species up to 13 PO<sub>4</sub> units can be resolved. HPLC has been successful for measuring the PO<sub>4</sub> chain-length distribution in a number of phosphate glasses.

#### References:

- Suzuya, K., D. L. Price, C.-K. Loong, and S. W. Martin (1998), "Structure of vitreous P<sub>2</sub>O<sub>5</sub> and alkali phosphate glasses:", *J. Non-Cryst. Solids*, **232-234**, 650.
- Van Wazer, J. R. (1958). *Phosphorus and Its Compounds*. New York: Interscience.