NETWORK TOPOLOGY AND PROPERTIES OF $\text{Na}_2\text{O-MO}_x\text{-P}_2\text{O}_5$ GLASSES : DISTINCTIVE FEATURES OF Zn^{2+} AND Bi^{3+}

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Abstract : The relationship between glass structure and MO_x content in $(100-2y)\text{NaPO}_3-y\text{MO}_x$ glasses, with $\text{M} = \text{Zn}^{2+}$ and Bi^{3+} , is described in terms of decondensation, reticulation and mixed network formation. The evolution of properties versus the MO_x content is related to this description of the glass network, and discussed from the P-O-M bond strength's values.

INTRODUCTION

The properties-composition relationships of phosphate glasses are often related to the electrostatic field strength (EFS) of the modifying cations, z/a^2 , where z is the charge, and a the ionic radius^{1,2}. The higher the electrostatic field strength, the higher the covalency of M-O(-P) bonds, which is reflected in a decrease of the coefficient of thermal expansion, the glass transition temperature, molar volume, helium permeability, and an increase of the aqueous durability. But some phenomena cannot be explained with this EFS approach : for instance the mixed alkali effect, or the non linear evolution of properties at the ultra to metaphosphate transition. An other approach has been proposed for a few years, based on a structural description of the glass network allowed by the progress in analytical techniques like Raman spectroscopy or Solid State Nuclear Magnetic Resonance (using Magic Angle Spinning). Brow³ used ^{31}P MAS-NMR to confirmed the phosphate groups repartition (Q^n) proposed by Van Wazer⁴ in the sixties. Stachel⁵ proposed an hypothesis for the anomalous behavior of the properties at the ultra - metaphosphate transition. Brow⁶ also used ^{27}Al and ^{31}P MAS NMR to elucidate the structural role of Al^{3+} in aluminophosphate glasses. These authors concluded that the properties depend not only on the EFS of the modifying elements, but also on the condensation of the phosphate network. Indeed, the addition of modifying cation to a glass results in P-O-P bonds breaking, with the formation of P-O-M bonds, so properties are also affected by the decondensation.

The aim of this paper is to discuss the evolution of properties of $(100-2y)\text{NaPO}_3-y\text{MO}_x$ glasses, with $\text{M} = \text{Zn}^{2+}$ ($x=1$) or Bi^{3+} ($x=3/2$). Zn^{2+} could be classified among network modifying elements, but its effect on phosphate glass properties is not clear : i) it was considered as an anomalous cation by Kordes⁷ in the description of properties near the ultra-metaphosphate transition, ii) it affects the helium permittivity of metaphosphate glasses in a non conventional manner⁸, and iii) it is reputed as a good agent for the improvement of phosphate glass durability⁹, whereas it lowers the glass transition

temperature. Bi^{3+} was chosen as a trivalent element with a high EFS, which is known to lead to an improvement of phosphate glasses properties (like Al^{3+}), for instance the aqueous durability¹⁰.

The system $(100-2y)\text{NaPO}_3-y\text{MO}_x$ is suitable for this structural approach because the linear chains of NaPO_3 allows an easy characterization of the glass network with ^{31}P NMR.

EXPERIMENTAL PROCEDURE

The $(100-2y)\text{NaPO}_3-y\text{MO}_x$ glasses were prepared from the appropriate amounts of NaPO_3 glass and ZnO or Bi_2O_3 . The molar percentage, y , varies from 0 to 33.3. The mixtures were melted in platinum crucibles for 1 hour at 1000°C , then quenched on a hot plate, and annealed. Glasses were analyzed for their Na_2O , P_2O_5 , and ZnO or Bi_2O_3 content. Glass transition temperature were determined from DSC experiments. The ^{31}P MAS-NMR spectra were recorded on a Bruker ASX100 spectrometer. Chemical shifts are expressed in ppm from $85\%\text{H}_3\text{PO}_4$, negative shifts being upfield. The spinning rate was 7 KHz. Q^n notation will be used : n is the number of bridging oxygens on a given phosphate group. The zinc coordination was determined from the absorption of Co^{2+} ions at 580nm, according to the method of Veinberg¹¹.

RESULTS AND DISCUSSION

Figure 1 shows the repartition of phosphate groups in the $(100-2y)\text{NaPO}_3-y\text{ZnO}$ glasses, determined from ^{31}P MAS-NMR spectra. The NaPO_3 glass contains only Q^2 sites, located at -20ppm. As ZnO is added to NaPO_3 , two kinds of Q^1 sites appear : the first is at -2.5ppm, it is attributed to Q^1 sites bonded to one zinc atom with octahedral coordination. Q^1 sites are created by the insertion of Zn ions in the metaphosphate chains : $\text{P-O-P} + \text{ZnO} \rightarrow \text{P-O-Zn-O-P}$. The second site is at -8.0ppm, it is attributed to Q^1 sites bonded to one zinc atom in tetrahedral conformation. This attribution is justified by the higher electrostatic field strength of tetrahedral zinc, which induces a higher shielding effect on the phosphorus nucleus¹². Some Q^0 sites are also detected at +9.1ppm in the glass with 33.3% ZnO . The site repartition shows that zinc ions exhibit a modifying character, as expected. 5 to 10% of phosphate groups are bonded to tetrahedral zinc, i.e with tighter bonds. Figure 2 shows that the relative amount of tetrahedral zinc remains low whatever the zinc content in the glass. Notice that the average chain length in the glass with 33.3% ZnO corresponds to only two phosphate units : it is a pyrophosphate glass. Tetrahedral zinc ions participate to the glass network, which enables the preparation of glass with as high as 33.3% ZnO without requirement to ultrafast quenching. The properties of $(100-2y)\text{NaPO}_3-y\text{ZnO}$ glasses can be related to the glass network model proposed above : Figure 3 shows the glass transition temperatures versus the ZnO content. A slight decrease is observed for ZnO content lower than 10%, it is attributed to the metaphosphate chain decondensation, as shown by the increase of Q^1 sites. Then the T_g increases with the ZnO content, showing the increase reticulation of the glass network, in accordance with the moderate EFS of Zn^{2+} ions. Contrary to the reported results⁶ for Al^{3+} , the presence of tetrahedral zinc ions does not lead to a levelling of T_g , probably owing to their small amount.

The introduction of Bi^{3+} ions in the sodium metaphosphate network also results in the formation of Q^1 and Q^1 sites, as shown by figure 4. Notice that Q^0 sites are detected at low Bi_2O_3 content, and that the Q^2 content remains rather high, even in the glass with

16% Bi₂O₃, which corresponds to a pyrophosphate composition. This can be explained by the site disproportionation reaction : $2Q^1 = Q^0 + Q^2$, which is shifted to the right when cations with high EFS are present¹³, like Bi³⁺. As glasses with pyrophosphate units can be prepared, a forming character can be attributed to Bi³⁺ ions. Although the coordination of Bi³⁺ ions in the glasses has not been determined, cristallochemistry concepts¹⁴ suggest that the coordination should not change with the concentration of Bi³⁺. More over, the glass transition temperature increases linearly with the Bi₂O₃ content (Figure 3) which also signifies that the coordination does not change. The glass network model for glasses containing Bi³⁺ is based on octahedral Bi³⁺ ions bonded to phosphate groups, but with an asymmetric coordination sphere : owing to the very high polarizability of Bi³⁺, four Bi-O bonds can be shorter, and participate to the glass network formation, and two bonds remain longer and bonded with a higher ionic character to phosphate groups.

SUMMARY

The phosphate glass network can be characterized from ³¹P MAS NMR spectra. The properties are dependent upon i) metaphosphate chain decondensation, ii) Q¹ site reticulation by cations with high EFS, and iii) mixed network formation for cation which can change or modify their coordination with oxygen. This last point constitutes the distinctive feature of Zn²⁺ and Bi³⁺ from conventional modifying cation.

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	Coordination	Z/a ²
Zn ²⁺	6	0.45
Zn ²⁺	4	0.53
Bi ³⁺	6	0.53
Al ³⁺	6	0.85
Al ³⁺	4	0.99
Ca ²⁺	6	0.36
Na ⁺	6/8	0.17

Electrostatic field strength (EFS) of some cations¹⁵, expressed in 10⁻¹⁰m⁻²

Figure 1 : Q^n groups distribution of the $(1-2y)\text{NaPO}_3 - y\text{ZnO}$ glasses.

Figure 2 : Average Zn^{2+} coordination in the $(1-2y)\text{NaPO}_3 - y\text{ZnO}$ glasses.

Figure 3 : Glass transition temperature of the $(1-2y)\text{NaPO}_3 - y\text{MO}_x$ glasses. Open symbols : $\text{M}=\text{Zn}^{2+}$, Closed symbols $\text{M}=\text{Bi}^{3+}$.

Figure 4 : Q^n groups distribution of the $(1-2y)\text{NaPO}_3 - y\text{Bi}_2\text{O}_3$ glasses.