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NMR STUDIES OF BOND ARRANGMENTS IN ALKALI PHOSPHATE GLASSES

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INTRODUCTION

Solid-state magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy has become a powerful tool for the investigation of local structure and medium range order in glasses. Previous ³¹P MAS NMR studies have detailed the local structure for a series of phosphate glasses [1-3]. Phosphate tetrahedra within the glass network are commonly described using the Qⁿ notation, where n = 0, 1, 2, 3 and represents the number of bridging oxygens attached to the phosphate. Using ³¹P MAS NMR different phosphate environments are readily identified and quantified. In this paper, we present a brief description of recent one dimensional (1D) ⁶Li, ⁷Li and ³¹P MAS experiments along with two-dimensional (2D) ³¹P exchange NMR experiments for a series of lithium ultraphosphate glasses. From the 2D exchange experiments the connectivities between different Qⁿ phosphate tetrahedra were directly measured, while the 1D experiments provided a measure of the P-O-P bond angle distribution and lithium coordination number as a function of Li₂O concentration.

EXPERIMENTAL

Preparation and handling of the anhydrous ultraphosphate glasses has been described previously in detail [4]. The MAS NMR experiments were performed on a Bruker AMX400 using a 4mm MAS probe at a resonant frequency of 162.0, 155.4 and 58.9 MHz for ³¹P, ⁷Li and ⁶Li respectively. The 2D exchange experiment utilized a radio frequency dipolar recoupling sequence (RFDR) as previously described [4]. The P-O-P bond angles were obtained from a non-linear deconvolution of the ³¹P MAS line shape assuming the relationships between ³¹P chemical shift and the P-O-P bond angle [5].

Qⁿ CONNECTIVITIES

The 2D RFDR NMR exchange experiments reintroduce the dipolar coupling between ³¹P nuclei and are directly proportional to 1/r³. Variation of the mixing time therefore provides a sensitive measure of the internuclear distance (r) between phosphate tetrahedra. It has been shown that for short mixing times the Qⁿ to Qⁿ exchange rate is governed by nearest neighbor interactions and is directly related to the number of Qⁿ species attached to a Qⁿ tetrahedron [4]. As an example, representative contour plots for 2D RFDR exchange experiments on the 35Li₂O•65P₂O₅ glass at zero mixing time and 2.56 ms mixing are shown in Fig. 1a and 1b, respectively. The off diagonal signal intensity in the 2.56 ms contour plot (Fig. 1b) clearly shows magnetization exchange due to nearest neighbor dipolar interactions. Simple quantitative information can be obtained by taking a 1D slice through the isotropic chemical shifts corresponding to different Qⁿ species. Figures 1c and 1d show the 1D slices taken through the Q² chemical shift (δ = -30.8 ppm) at 0 ms and 2.56 ms mixing times. At zero mixing time (Fig. 1c) only a narrow Lorentzian line is observed representing non-exchange magnetization. At 2.56 ms (Fig. 1d) the Q² cross section shows three resonances: (1) a narrow Lorentzian for the non-exchanging Q² magnetization, Q²(0), (2) a broad resonance at δ = -30.8 ppm resulting from Q²→Q² exchange and (3) another broad resonance at δ = -44.1 ppm resulting from Q²→Q³ exchange. Similarly, the slice through the Q³ chemical shift at δ = -44.1 ppm (Figs. 1e and 1f) can also be deconvoluted into three overlapping resonances as seen in the insets.

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Figure 1. 2D RFDR ^{31}P MAS NMR exchange contour plots for the $35\text{Li}_2\text{O} \cdot 65\text{P}_2\text{O}_5$ glass at a) 0 ms and b) 2.56 ms mixing times. Cross sections were taken through the isotropic resonance corresponding to the different Q^n species for different mixing times: c) Q^2 $\delta = -30.8$ ppm, $\tau_{\text{mix}} = 0.0$ ms, e) Q^3 , $\delta = -44.1$ ppm, $\tau_{\text{mix}} = 0.0$ ms d) Q^2 $\tau_{\text{mix}} = 2.56$ ms, f) Q^3 $\tau_{\text{mix}} = 2.56$ ms. Each mixing time is plotted on the same relative intensity scale. For this glass composition the exchange is almost equally distributed between different Q^2 - Q^3 , Q^3 - Q^3 and Q^2 - Q^2 connectivities (inset).

The relative areas of these exchange cross peaks can be compared to the connectivity distributions predicted for different glass structural models. For example, the relative exchange functions observed experimentally compare well to those predicted for a glass that has undergone random depolymerization as shown in Fig. 2 [4]. Contrast this to the exchange functions that would result from a glass containing highly segregated Q^3 and Q^2 domains (microdomains). In the case of microdomains the $Q^3 \rightarrow Q^3$ and $Q^2 \rightarrow Q^2$ transfer functions would be predicted to be near unity for large regions of Li_2O concentrations (all nearest neighbors of same Q^n type). From inspection of Fig. 2, it is clear that this was not observed experimentally, precluding microdomain formation in the lithium ultraphosphate glasses presented here.

Figure 2. Theoretical transfer functions ($Q^n \rightarrow Q^n$) assuming a randomly depolymerized model in a binary phosphate glass versus experimental (●,○) NMR transfer functions obtained from 2D RFDR ^{31}P MAS NMR exchange experiments for $xLi_2O \cdot (1-x)P_2O_5$ glasses.

Table 1: ^{31}P NMR Chemical Shifts, Line Widths, Homogenous Line Widths ($\Delta\nu$) and Bond Angle Distribution Widths ($\Delta\theta$) For Various $xLi_2O \cdot (1-x)P_2O_5$ Glasses.

Glass/Resonance	δ_{iso} (ppm)	FWHM (Hz)	$\Delta\nu$ (Hz)	$\Delta\theta$ (deg)
P_2O_5				
Q^3	-52.9	2137	46	24
$15Li_2O \cdot 85P_2O_5$				
Q^3	-51.8	2380	34	28
Q^2	-34.5	1380	30	25
$35Li_2O \cdot 65P_2O_5$				
Q^3	-44.1	2530	20	23
Q^2	-30.8	1850	35	28
$43Li_2O \cdot 57P_2O_5$				
Q^3	-40.0	2274	20	20
Q^2	-24.7	1703	45	26
$50Li_2O \cdot 50P_2O_5$				
Q^2	-23.56	1186	64	15
$55Li_2O \cdot 45P_2O_5$				
Q^2	-23.5	1580	46	19
Q^1	-5.6	1030	38	20

P-O-P BOND ANGLE DISTRIBUTIONS

In addition to the measurement of tetrahedra connectivities, additional structural parameters of the glass can be obtained from ^{31}P MAS NMR. It has been argued that the wide line widths observed in the ^{31}P MAS NMR experiments (Table 1) do not result from homogenous broadening, but instead arise from inhomogenous broadening due to variations in the P-O-P bond angle and P-O bond lengths that produce small changes in the chemical shift. The 2D experiments presented in Fig. 1 confirm this argument, clearly showing that for a given frequency the homogenous line width is quite narrow. Additional rotor-synchronized two pulse Hahn echo (TPHE) experiments have determined the homogenous line width vary between 0.1 to 0.3 ppm for the entire Li_2O range investigated and are much narrower than the observed 1D line widths. Using the semi-empirical relationships between ^{31}P chemical shift and changes in the P-O-P bond angle [5] the P-O-P bond angle distributions were obtained, and are shown in Fig. 3.

Figure 3. The P-O-P angle (θ) distributions for the $\text{Li}_2\text{O} \cdot \text{P}_2\text{O}_5$ glasses. The mean angle predicted from *ab initio* calculations (●) for the Li metaphosphate (50:50) [6] is shown for comparison.

The agreement between the mean P-O-P bond angle (θ) and those predicted from *ab initio* calculations for the lithium metaphosphate (50:50) [6] are good, while the mean angle for the Q^3 tetrahedra in P_2O_5 differs significantly than that reported for the X-ray structure of crystalline P_2O_5 . This discrepancy suggest that the Q^3 chemical shift relation provided by Sternberg et al. [5] may need additional refinement. The experimental P-O-P bond angle distributions in Fig. 3 provide a critical benchmark for future computer modeling. The full width at half maximum of these bond angle distributions ($\Delta\theta$) as a function of mole fraction Li_2O can also be used as a matrix of changes in glass structure.

These variations in $\Delta\theta$ together with changes in the glass transition temperature (T_g) are shown in Fig. 4. At low Li_2O content there is an initial disruption of the 3D phosphate network as seen by a small increase in $\Delta\theta$. As the glass approaches the metaphosphate concentration there is a reduction in $\Delta\theta$ for both Q^3 and Q^2 , suggesting an increase in the structural order with increasing Li_2O concentration. The phenomena responsible for this increased ordering is still under investigation.

Figure 4. P-O-P bond angle distribution ($\Delta\theta$) with Li_2O content in the lithium phosphate glasses. Lines are drawn as guides for the eye.

LITHIUM COORDINATION

The local structure for the alkali modifiers can be investigated using NMR for a variety of nucleus. Determination of the chemical shift for the modifying cation in glasses has been shown to be strongly influenced by the number of oxygens in the first coordination sphere. These chemical shift variations have been observed for ^6Li , ^7Li , ^{23}Na , ^{25}Mg and ^{27}Al NMR [2,3,7]. By combining ^6Li and ^7Li MAS NMR investigations for the ultraphosphate glasses discussed here, changes in the local coordination of the lithium cation were addressed.

Representative solid state MAS NMR spectra for lithium ultraphosphate glasses are shown in for ^7Li (Fig. 5a) and for ^6Li (Fig. 5b). Both ^7Li ($I = 3/2$) and ^6Li ($I = 1$) are quadrupolar nuclei requiring determination of the quadrupolar shift in order to obtain true chemical shift information. For the ultraphosphate glasses the quadrupolar interaction is small enough such that second order quadrupolar line shape perturbations were not observed. Inspection of Fig. 5a shows a strong central resonance (resulting from the $\pm 1/2 \leftrightarrow \mp 1/2$ transition) with a sideband manifold due to the $\pm 3/2 \leftrightarrow \pm 1/2$ transitions. The first order quadrupolar interaction has no effect on the central transition while the second order quadrupolar shift for the $m \leftrightarrow m$ transition in ppm is defined by

$$\delta_{iso}^{(2Q)} = -\frac{3}{40} \frac{C_Q^2}{\nu_L^2} \frac{(I(I+1)-3-9m(m-1))}{I^2(2I-1)^2} \left(1 + \frac{\eta_Q^2}{3}\right) \times 10^6 \quad (1)$$

where C_Q is the quadrupolar coupling constant, η_Q is the quadrupolar asymmetry parameter and ν_L is the Larmor frequency. The observed shift in the MAS spectra is then given by the sum of the chemical shift and this second order isotropic shift

$$\delta^{obs} = \delta^{CS} + \delta_{iso}^{(2Q)} \quad (2)$$

For ^6Li (Fig. 5b) only a single resonance was observed resulting from the $\pm 1 \leftrightarrow 0$ transition, again with the second order quadrupolar isotropic shift given by Eqn. 1. Because the quadrupolar moment of ^6Li is $\sim 1/50$ that of ^7Li [7] the magnitude of the second quadrupolar shift to the observed shift is negligible. This results in the observed ^6Li shift observed in the MAS spectra (Fig. 5b) being a close approximation for the true chemical shift. The difference between the shifts observed in the ^7Li and ^6Li Mas spectra provide a measure of the quadrupolar coupling constant (C_Q) using Eqns. 1 and 2. For the lithium ultraphosphate glasses the shift difference at 9.4 Tesla were very small (< 0.1 ppm which is approximately the resolution limit due to line width) providing an upper limit of approximately 0.5 MHz for the quadrupolar coupling constant. A more accurate estimate of C_Q as a function of Li modifier concentration could be obtained from the inverse proportionality of the quadrupolar shift to ν_L^2 . Determination of the ^7Li shifts at different field strengths are presently being pursued.

Figure 5. Representative a) ^7Li and b) ^6Li MAS NMR for $x\text{Li}_2\text{O} \cdot (1-x)\text{P}_2\text{O}_5$ glasses. The ^7Li spectra shows a strong central resonance for the $\pm 1/2 \leftrightarrow \mp 1/2$ transition and a spinning sideband manifold resulting from the $\pm 3/2 \leftrightarrow \pm 1/2$ transitions. The ^6Li spectra shows only a single resonance, with a negligible second order quadrupolar shift, providing a good approximation of the true chemical shift. The variation of the ^6Li chemical shift (inset) versus Li_2O concentrations reveals a continuous decrease in the Li coordination number.

Fig. 5b (inset) shows the ^6Li chemical shift variation as a function mole percent Li_2O added to the glass. A linear increase in the chemical shift with increasing mole fraction is observed. Additional glass with compositions in the critical region between 20 and 30 mole percent Li_2O are being prepared to better define this trend near the minimum T_g region. In silicate glasses increases in the chemical shift have been correlated to a decrease in the coordination number of the lithium.[7] Similar changes in the chemical shift have been reported for ^{27}Al , ^{23}Na and ^{25}Mg . For the lithium ultraphosphate glasses the chemical shift variations correspond to the Li coordination changing from LiO_6 in the $15\text{Li}_2\text{O}\cdot 85\text{P}_2\text{O}_5$ glass towards increasing amounts of LiO_5 and LiO_4 species at higher Li_2O concentrations. This trend in ^6Li chemical shift with changing Li_2O concentration does not suggest the formation of microdomains, and supports the random depolymerization structural model discussed above. It is true that the correlation reported for lithium silicate glasses [7] may not be directly applicable to the lithium phosphate glasses discussed here, necessitating future investigation of lithium coordination in crystalline phosphate systems.

CONCLUSIONS

The results from several different types of NMR experiments have been present, and provide examples of the types of structural information that can be obtained using NMR techniques. The ability to probe medium range order using NMR exchange experiments was also demonstrated, and demonstrates the applicability of multi-dimensional NMR techniques to probe structure in amorphous glasses and complex ceramics.

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