

A ^{31}P -NMR Study of Borophosphate Glasses

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It is shown that ^{31}P nuclear magnetic resonance (NMR) spectroscopy with magic angle spinning (MAS) discriminates among different types of PO_4 units occurring in borophosphate glasses. The isotropic ^{31}P chemical shift of the PO_4 increases by nearly 70 ppm in going from the "branching unit," neutral and covalently bonded, to the "monomeric unit," which carries a -3 nominal charge. By using both stationary and MAS ^{31}P spectra, we also obtain the average values, and distribution widths, for chemical shift anisotropy and the asymmetry factor of PO_4 units occurring in vitreous borophosphates. Analysis of these NMR spectra provides detailed information about the short-range order in these glasses. It is also shown that the ^{31}P -NMR-MAS technique may contribute significantly to phase separation and crystallization studies of phosphorus-containing glasses. © 1987 Academic Press, Inc.

In the traditional sense, phosphates are compounds in which the P atoms are coordinated to four oxygen atoms (phosphate units) (1). High-resolution ^{31}P -NMR studies, both in the liquid and in the solid state, have greatly contributed to our knowledge of the coordination of the phosphate units in phosphate esters (2) and in substances of biological interest (3, 4). On the other hand, NMR studies of condensed phosphates are relatively scarce (5), since an understanding of the complex ^{31}P spectra requires application of magic angle spinning (MAS) techniques. Grimmer and Haubenreisser

(6) have characterized the chemical shift tensor of phosphorus in crystalline potassium phosphates, while Duncan and Douglass (7) have analyzed the spectra of sodium and aluminum phosphates and of a phosphosilicate glass. We have recently applied the ^{31}P -NMR-MAS technique (8) in structural studies of fast ion-conducting borophosphate glasses. We will show that, in these glasses, this technique may provide information about chemical composition, as well as about phase separation and crystallization phenomena. We will also give the results of an analysis of the stationary ^{31}P -NMR spectra of these glasses, which provides, for several phosphate units, characteristic values of chemical shift anisotropy and asymmetry factor.

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The spectra have been collected at room temperature with Nicolet spectrometers and two Nalorac superconducting magnets, energized at 3.6 and 8.5 Tesla, respectively. The home-built spinner, of the Andrew-Beams type, was made of Delrin. In the MAS experiments, the sidebands were identified by comparing spectra with different spinning rates, between 1500 and 5000 Hz. All ^{31}P spectra will be referenced to 85% H_3PO_4 .

The MAS spectrum of a commercial Graham's salt (9) can be decomposed into three components (Fig. 1). The main peak, A, is certainly due to the middle units Na^+PO_4^- (or $-\text{O}-\text{NaPO}_2-\text{O}-$). Peak C occurs at 1 ppm, which suggests its assignment to the end unit $-\text{O}-\text{Na}_2\text{PO}_3$. In fact, the signals of end units in crystalline sodium phosphates apparently occur in the (+4.8, -2.4) ppm interval (7, 10). By the way, in our experience, the average shift of the end unit is strongly dependent on the cation: in lithium phosphate glasses it occurs around -5 ppm, while in silver phosphates it is observed at 7 ppm. We have analyzed a commercial sample of hydrated HPO_3 , in which the end signal occurs at -7 ppm (11). Since position of peak B (-5 ppm) of Fig. 1 is intermediate between that of Na^+ -bonded and H^+ -bonded end units, it is suggested that it is primarily due to end units of the type $-\text{O}-\text{NaHPO}_3$, or to end units coordinated to both Na^+ and H^+ . Within $\pm 0.5\%$ the relative intensities of peaks A, B, and C

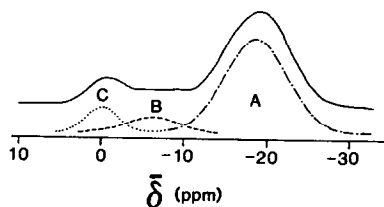


FIG. 1. The full curve is the ^{31}P -MAS spectrum of sodium metaphosphate powder. The curves represent the decomposition of the spectrum into Gaussian components (see text).

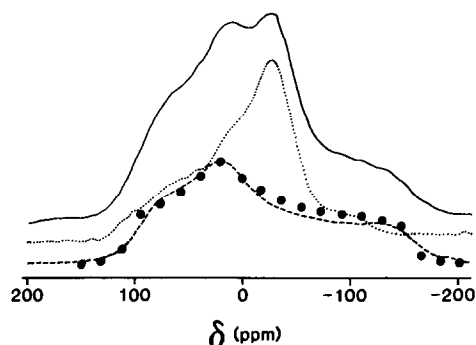


FIG. 2. Stationary spectrum of the $\text{Ag}_2\text{O} \cdot (0.71)\text{P}_2\text{O}_5$ glass (solid line), which is decomposed into a pattern of middle units (dashed line) and end units (dotted line) through comparison of spectra with different [end unit]/[middle unit] ratios. Circles represent the simulation of the middle unit component with the parameters given in Table I.

are 80, 10, and 10%, respectively. If our assignments are correct, it follows that the actual composition of this Graham's salt is $(20)\text{NaPO}_3 \cdot \text{Na}_2\text{O} \cdot \text{H}_2\text{O}$, the phosphate chain is 10 units long (in fair agreement with the length corresponding to the nominal composition), and the water content is about 0.8 wt%. This figure should be compared with the 0.4 wt% of water found by Gray and Klein in the driest form of sodium metaphosphate they were able to obtain (12).

Figure 2 (solid line) shows the stationary spectrum of a phosphate glass with 60% of phosphorus belonging to middle units, and the remaining 40% belonging to end units. After proper normalization of the intensities, we subtracted from this spectrum the stationary signal of vitreous AgPO_3 (dashed curve, middle units) and obtained the dotted curve (end unit). This subtraction procedure postulates that, with changing glass composition, the powder pattern of a phosphate remains essentially the same. Furthermore, for the glasses that we are comparing, we should be able to determine accurately, through MAS experiments, the fractions of the different phosphate units. While a MAS peak yields directly the distri-

bution of the isotropic shift $\bar{\delta}$, rough average values for the tensor principal components, δ_1 , δ_2 , and δ_3 , can be obtained from the peaks and shoulders of a stationary spectrum. We have simulated the stationary spectra by assuming that the anisotropic shift, $\Delta\delta = \frac{2}{3}(\delta_1 - \delta)$, has a Gaussian distribution, independent of that of $\bar{\delta}$. The agreement between experimental and simulated spectra improves substantially when the pattern due to chemical shift effects is convoluted with a Gaussian broadening function. The full width at half height (FWHH) of such a function was in the kilohertz range, which is consistent with an order-of-magnitude evaluation of the dipolar broadening and the results of Duncan and Douglass (7). We have to mention that, in several cases, we were unable to obtain a decent fit of the "experimental" spectrum, the possible reason being the inadequacy of the subtraction procedure, or a non-Gaussian distribution of the chemical shift components. No standard routine to optimize the fit has been used. Rather, we wrote an interactive graphic program which displays simulated and experimental spectra and

narrowed their differences by trial and error.

With the procedure outlined above, we succeeded in characterizing the chemical shift tensor of several units occurring in the borophosphate glasses. Table I lists our results. Here, we give the average values ($\langle \delta \rangle$) of $\bar{\delta}$, $\Delta\delta$, and the asymmetry parameter η , together with their standard deviations σ . The unit designated MB1 is observed in the borophosphate glasses and is believed to consist of a metaphosphate unit with one of the bridging oxygens bonded to a borate unit: P-[O-PO₂-O]-B. The existence of this unit has been suggested by the behavior of the ³¹P spectra when boron oxide is progressively substituted to phosphorus oxide in a Ag₂O · P₂O₅ glass. Up to a boron fraction $y = B/(B + P) = 0.4$, the MAS spectrum has a dominant peak (intensity >80%) in the middle region, which undergoes some changes in width and position (from ~ -18 to ~ -16 ppm) as the boron content increases. The changes of the stationary spectrum caused by boron addition are more substantial. In particular, the intensity of the shoulder around -170 ppm

TABLE I
CHEMICAL SHIFT TENSORS OF PHOSPHATE UNITS

Unit	Cation	$\bar{\delta}$ (ppm)		$\Delta\delta$ (ppm)		η	
		$\langle \bar{\delta} \rangle$	$\sigma(\bar{\delta})$	$\langle \Delta\delta \rangle$	$\sigma(\Delta\delta)$	$\langle \eta \rangle$	$\sigma(\eta)$
Branching	Li	-42	5	- ^a		- ^a	
Middle	Ag	-17.9	4.5	-155	10	0.56	0.05
Middle	Li	-23.9	4.7	-138	10	0.54	0.06
End	Ag	6.7	2.4	90	5	0.07	0.04
End	Li	-4.1	3.3	95	7	0.05	0.04
MB1	Ag	-16.5	6.9	-100	14	0.85	0.16
MB2	Ag	~ -2	~4	- ^a		- ^a	
EB	Ag	~12	~3	- ^a		- ^a	
Monomer ^b	Ag	28.5	0.6	~0	~0	~0	~0
Monomer	Li	8	1.5	- ^a		- ^a	
BPO ₄ ^c		-30.6	1.2	40	2.5	0.9	0.07

^a Not determined.

^b Partially crystallized.

^c Crystalline.

($\sim\delta_3$) (Fig. 2), which is a high-field feature characteristic of the phosphate middle units (7), reduces rapidly and has completely disappeared when $y = 0.4$. In glasses with a boron content >0.4 , position and width of the MAS peak in the middle region no longer change, confirming that the phosphate middle units have been fully converted into another unit, with δ in the middle region, but with values of $\Delta\delta$ and η substantially different from those of the phosphate middle unit (see Table I).

By analyzing the MAS spectra of many silver borophosphates, we found that addition of boron causes the appearance of two well-resolved peaks near -2 and $+12$ ppm, which are assigned to an MB2 unit ($B-AgPO_4-B$) $B-[O-PO_2-O]-B$ and to an EB unit ($B-Ag_2PO_4$), respectively. These units are listed in Table I, but a determination of their chemical shift anisotropy and asymmetry has not been attempted, since it required repeated application of the subtraction procedure to stationary spectra.

When the ^{31}P -MAS spectra are broad and featureless, like those of the lithium borophosphate glasses reported in Fig. 3, a decomposition procedure is difficult, or meaningless. With reference to Fig. 3, we can generically say that, with increasing bo-

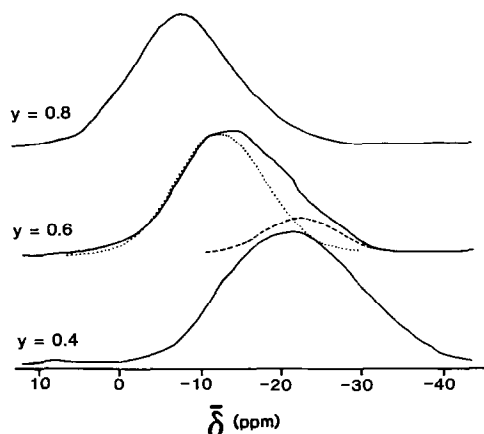


Fig. 3. MAS spectra of the $(0.5)Li_2O \cdot (y)B_2O_3 \cdot (1-y)P_2O_5$ glasses, with $y = 0.4$, $y = 0.6$, and $y = 0.8$.

ron content, the spectrum shifts downfield because of a progressive conversion of middle and branching phosphate units into MB1-MB2 units and EB units. However, the spectrum of the glass with a ratio $B/B + P = 0.6$ is asymmetric enough to allow isolation of a contribution (dashed line in Fig. 3) which occurs at the position of the signal in the $LiPO_3$ glass. Such a spectral feature cannot be isolated in either the glass richer in boron ($y = 0.8$) or the one richer in phosphorus ($y = 0.4$). This fact could be explained if, in the $y = 0.6$ glass, a phase-separated lithium metaphosphate existed. The Raman spectra of the glass with $y = 0.6$ has a peak at 775 cm^{-1} , typical of the boroxol rings, which is absent in the $y = 0.4$ and $y = 0.6$ glasses (8). Thus, both ^{31}P -NMR and Raman spectroscopies suggest that lithium borophosphates with $[B + P]/[Li] = 2$ are partially immiscible near $y = 0.6$.

The ^{31}P -MAS peaks of vitreous phosphates have typical FWHH values in the ~ 10 -ppm range, which is attributed to the spread of chemical shifts induced by the disorder. In partially crystalline phosphates, such as the BPO_4 compound (13), the widths of the ^{31}P -MAS lines are substantially smaller (see the column in Table I). It follows that the ^{31}P resonance is well suited to investigate crystallization phenomena in glasses. As a matter of fact, the sharpest peak in Fig. 4, which is due to the Ag_3PO_4 species (monomeric unit), has been obtained in a silver borophosphate glass where no Bragg peaks are seen by X-ray diffraction. This assignment is supported by the MAS spectra of partially crystallized samples where the presence of silver orthophosphate has been confirmed by X rays.

In conclusion, the chemical shift components of the phosphate units in glasses have characteristic average values and distribution widths and a combined use of ^{31}P stationary and spinning spectra often allows unambiguous identification of the "finger-

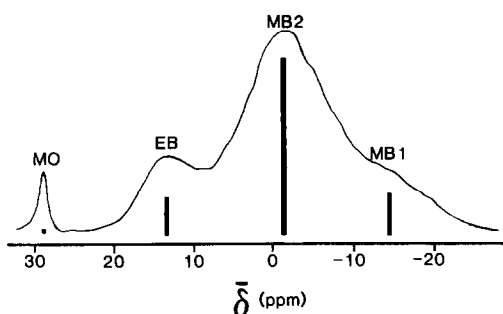


FIG. 4. MAS spectrum of the $\text{Ag}_2\text{O} \cdot (1.6)\text{B}_2\text{O}_3 \cdot (0.4)\text{P}_2\text{O}_5$ glass. The leftmost peak is due to crystallized silver orthophosphate (MO = monomeric unit). The vertical bars are proportional to the intensities of the Gaussian components into which the MAS spectrum is decomposed.

prints" of these units. We have given chemical shift data on lithium and silver phosphate units, which compare well with the values reported in the literature for sodium and potassium phosphates (6, 7, 10), and have identified the spectral contribution of phosphate units bonded to borons. Attention has been called to the potential applications of ^{31}P -NMR techniques to analytical characterization of condensed phosphates and to phase separation and crystallization studies.

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