HIGH-RESOLUTION ^{27}Al - ^{31}P DOUBLE RESONANCE SOLID-STATE NMR STUDIES OF ALUMINOPHOSPHATE GLASSES

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Abstract Modern high-resolution NMR spectroscopic techniques were applied to study the local environments and site connectivities present in various glassy aluminophosphates. Through the combined application of complementary magic-angle spinning (MAS), ^{27}Al triple-quantum MAS (TQMAS), as well as cross-polarization MAS (CPMAS) and rotational echo double resonance (REDOR) methods, a comprehensive picture concerning the *short-* and *intermediate-range order* has been developed for the titled glasses.

INTRODUCTION

Alkali- and alkaline-earth phosphate glasses have proven their utility in a variety of technical applications, including their use in high-expansion, low-temperature glass-to-metal seals.¹ To improve the mechanical, thermal and chemical durabilities of these materials, alumina is frequently added as a third component.^{2,3} With the goal of understanding this effect, the local structure of aluminophosphate glasses has been investigated, including studies by photoelectron spectroscopy and solid-state nuclear magnetic resonance (NMR).^{4,5} Application of standard NMR methodology (magic-angle spinning, MAS) to these systems has resulted in detailed information about the immediate nearest neighbor environments of the network-former species. Using ^{31}P and ^{27}Al MAS-NMR as a function of glass composition, Brow and coworkers concluded that in sodium aluminophosphate glasses the phosphorus sites are mostly present in the form of various different types of meta-, pyro-, and orthophosphate environments, whereas aluminum can basically occur in four-, five-, six-coordinations.^{4,5} Specifically, the spectra indicate that in most of the materials within the glass-forming region the

majority of aluminum sites are six-coordinated. This finding is somewhat surprising in view of the isoelectronic relationship between AlPO_4 and SiO_2 , both of which have tetrahedrally coordinated structures in their crystalline states. The incomplete $\text{SiO}_2 \leftrightarrow \text{AlPO}_4$ analogy has been discussed on the basis of bond valence arguments,^{5,6} leading to the prediction that the mean aluminum coordination number should depend on the oxygen to phosphorus ratio in ternary alkali aluminophosphate glasses. These predictions are indeed confirmed by the experimental results: For example, along the join $(\text{Al}_2\text{O}_3)_x(\text{NaPO}_3)_{1-x}$, the fraction of tetrahedral aluminum increases systematically with increasing alumina content x , at the expense of the fraction of octahedral aluminum.⁴

While simple MAS-NMR is well-able to identify and quantitate the various nearest-neighbor environments (*short range-order*) present in these glasses, the technique is silent about the more intricate question of how these units are connected in forming the overall glassy network. To obtain a deeper-level understanding of *intermediate-range order* in aluminophosphate glasses, it would be very important to learn how the various aluminum sites are bonded to the different phosphorus species present. It is the central goal of this work to apply the cross-polarization MAS⁷ (CPMAS) and rotational echo double resonance⁸ (REDOR) techniques to probe the spatial distribution of the aluminum and phosphorus units. The feasibility of such heteronuclear double resonance studies in glasses was independently illustrated by Herzog *et al.*⁹ and van Wüllen *et al.*¹⁰ and was extended later to aluminophosphate glasses with more complex chemical compositions.¹¹ In the present study we aim to illustrate that these techniques also provide quantitative information on the basis of which compositional trends can be discussed.

EXPERIMENTAL PROCEDURE

Sodium phosphate glass was first prepared by melting crystalline sodium metaphosphate in an alumina crucible at 800 °C for one hour. The melt was quenched and then mixed with aluminum oxide to form the desired glass batches. The mixture was heated at 1400 °C in a Pt crucible for one hour and then poured onto a water-cooled

copper block. The glass products were stored in desiccator. Table 1 summarize the batch compositions of the sodium aluminophosphate glasses under study.

All the NMR measurements were carried out at 130.3 and 202.5 MHz for ^{27}Al and ^{31}P , respectively, on a Bruker DSX-500 spectrometer. The isotropic chemical shifts of ^{27}Al and ^{31}P are referenced to 1M aqueous AlCl_3 and 85% H_3PO_4 solutions, respectively. The CPMAS spectra were measured under the following conditions: spinning speed 10 kHz; relaxation delay 0.5 s; contact time 2 ms; ^{27}Al nutation frequency 2.4 kHz; ^{31}P nutation frequency 7.1 kHz. The experimental setup of the triple-quantum MAS (TQMAS)¹² experiments has been described previously.¹³ A detailed discussion on the experimental aspects of $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR studies will be published separately.¹⁴

TABLE 1 Compositions and glass transition temperatures of the glasses under study.

Samples	Batch composition [mol %]	T_g [°C]
	$\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5$	
NAP5	47.5-5-47.5	437
NAP10	45-10-45	438
NAP20	40-20-20	456

RESULTS AND DISCUSSION

The ^{31}P and ^{27}Al MAS spectra are illustrated in Figure 1. Accurate ^{27}Al chemical shifts and second-order quadrupolar shifts were obtained by TQMAS experiments and are reported in Table 2 (spectra not shown). The assignment of the ^{27}Al signals have been established in the literature on the basis of their chemical shift ranges.⁵ In accordance to the results of Brow *et al.*, the fraction of AlO_4 increases systematically with increasing alumina content, at the expense of the fraction of AlO_6 .⁵ On the other hand, it is clearly shown that the ^{31}P chemical shifts increase as the Al_2O_3 content increases from NAP5 to NAP20 while the opposite is true for the ^{31}P chemical shift anisotropies which indicates that the first coordination spheres for the phosphorus units become more symmetric with increasing aluminum content.

FIGURE 1. ^{27}Al and ^{31}P MAS spectra of the studied glasses at a spinning speed of 10 kHz. Spinning sidebands are marked with asterisks.

To explore the spatial proximities among the various aluminum and phosphorus units, $^{31}\text{P}\{^{27}\text{Al}\}$ CPMAS experiments were conducted. The power level for the ^{27}Al channel was adjusted to allow a selective spinlocking for a particular aluminum coordination unit.¹⁵ By this strategy it is possible to distinguish the spatial proximity between phosphorus units and the three different aluminum units (AlO_4 , AlO_5 , AlO_6). In the absence of a quantitative theory for the CP dynamics involving quadrupolar nuclei, the CP rate between ^{27}Al and ^{31}P is roughly approximated by a linear regression analysis of signal intensities measured at short CP contact times as illustrated by Figure 2 for the glass sample NAP20. The selective CP rates of $^{31}\text{P}\{^{27}\text{AlO}_4\}$, $^{31}\text{P}\{^{27}\text{AlO}_5\}$ and $^{31}\text{P}\{^{27}\text{AlO}_6\}$ determined in this fashion were found to be identical within experimental error (Table 2), showing that AlO_4 , AlO_5 and AlO_6 are well-integrated into the glass structure by phosphorus links. Based on the chemical shift data of the $^{31}\text{P}\{^{27}\text{Al}\}$

CPMAS measurements, the high-frequency components of the ^{31}P MAS spectra (*viz.* peaks at -6.8, -6.1 and -3.2 ppm) belong to P-O-P species while the low-frequency components arise from the phosphorus tetrahedra surrounded by aluminum species. The spectral editing capability of $^{31}\text{P}\{^{27}\text{Al}\}$ CPMAS-NMR is illustrated in the inset of Figure 2.

FIGURE 2. $^{31}\text{P}\{^{27}\text{Al}\}$ CPMAS experiments with variable contact times for the NAP20 glass. The AlO_4 unit was selectively spinlocked. The inset shows the corresponding MAS (upper trace) and CPMAS (lower trace). The arrow indicates the position of the shoulder component which is not found in the CPMAS spectrum, demonstrating the spectral editing feature of the CPMAS experiment.

TABLE 2 Summary of the ^{31}P MAS and $^{31}\text{P}\{^{27}\text{Al}\}$ CPMAS results.

		NAP5	NAP10	NAP20
^{31}P :	δ_{iso} [ppm]	-6.8	-6.1	-3.2
		-14.6	-13.7	-11.9
$^{31}\text{P}\{^{27}\text{AlO}_4\}$:	δ_{iso} [ppm]	-13.1 ± 0.2	-13.1 ± 0.1	-11.6 ± 0.1
	T_{cp}^{-1} [s^{-1}]	600 ± 100	650 ± 30	600 ± 20
$^{31}\text{P}\{^{27}\text{AlO}_5\}$:	δ_{iso} [ppm]	-13.1 ± 0.2	-13.6 ± 0.1	--
	T_{cp}^{-1} [s^{-1}]	590 ± 100	580 ± 30	
$^{31}\text{P}\{^{27}\text{AlO}_6\}$:	δ_{iso} [ppm]	-15.4 ± 0.1	-13.5 ± 0.1	--
	T_{cp}^{-1} [s^{-1}]	690 ± 30	600 ± 25	

More quantitative information on the distances between Al and P units is provided by $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR measurements. It has been shown that the S-I_n REDOR dephasing curves for short evolution time (NT_r) can be approximated by a simple analytical function:^{16,17}

$$\frac{\Delta S}{S_0} = \frac{4}{3\pi^2} M_2^{\text{IS}} (NT_r)^2 \quad (1)$$

where M_2^{IS} is the heterodipolar second moment. The experimental M_2^{IS} values can be contrasted with theoretical values for any real or hypothetical structural models using van Vleck theory.¹⁸ This strategy has been verified by measurements on crystalline $\text{Al}(\text{PO}_3)_3$ and AlPO_4 , where the $M_2^{\text{Al-P}}$ data measured were found in satisfactory agreement with the calculated values based on the crystallographic structures (see Table 3). The $M_2^{\text{Al-P}}$ data for the studied glasses were extracted by fitting Eq (1) to the initial $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR dephasing curves as shown in Figure 3 and the results are summarized in Table 3. Accordingly, all the ^{27}Al - ^{31}P second moments measured for the glasses are of the same order of magnitude, illustrating that the local fields exerted by the closest ^{31}P neighbors at the various aluminum sites are roughly comparable within each glass sample. In other words, the *intermediate-range order* in the glasses is dominated by Al-O-P connectivities. A closer inspection of the data reveals that the $M_2^{\text{Al-P}}$ value for the AlO_4 unit in NAP20 is very close to that measured in crystalline AlPO_4 , consistent with a structure in which the AlO_4 units covalently link to PO_4 units

as in the crystalline reference compound. As the P/Al ratio increases with the series NAP20 $\rightarrow$ NAP10 $\rightarrow$ NAP5 the M_2^{Al-P} values associated with the AlO_4 groups increase monotonically. We attribute this effect not to changes in connectivity but rather to the increased dipolar contribution of further remote ^{31}P nuclei as the phosphorus density of the glass is increased. The M_2^{Al-P} values associated with the AlO_5 and AlO_6 groups are comparable to the value measured in crystalline $Al(PO_3)_3$, indicating a similar local environment.

FIGURE 3 $^{27}Al\{^{31}P\}$ REDOR dephasing curve for the AlO_4 site of NAP20.

TABLE 3 Summary of the ^{27}Al TQMAS and $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR results

Samples		δ_{iso} [ppm]	SOQE ^a [MHz]	$M_2^{\text{Al-P}}$ [10^6 s^{-2}]
AlPO ₄ :	AlO ₄	41.5	1.6	4.6 ± 0.1 (5.64 ^b)
Al(PO ₃) ₃ :	AlO ₆	-21.6	0.22	5.4 ± 0.1 (6.46 ^b)
NAP5:	AlO ₄	50.6	3.9	6.5 ± 0.3
	AlO ₅	19.2	4.0	5.3 ± 0.2
	AlO ₆	-10.4	3.0	5.9 ± 0.1
NAP10:	AlO ₄	51.2	3.9	5.3 ± 0.1
	AlO ₅	18.0	3.9	5.5 ± 0.2
	AlO ₆	-11.5	2.9	6.1 ± 0.3
NAP20:	AlO ₄	50.0	3.6	4.4 ± 0.1
	AlO ₅	15.2	3.6	--
	AlO ₆	-8.1	2.9	--

^a Second order quadrupolar effect is defined as $\frac{e^2 q Q}{h} \sqrt{1 + \frac{\eta_Q^2}{3}}$. ^b Calculated second moment values based on crystallographic data,^{19,20} considering the nearest neighbor environments only.¹⁶

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