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Using ^{27}Al , ^{31}P MAS and $^{31}\text{P}/^{27}\text{Al}$ and $^{31}\text{P}/^{23}\text{Na}$ TRAPDOR NMR Spectroscopies to Study Sodium Aluminophosphate Glasses

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Introduction

A series of NAP glasses along the compositional tie line $x\text{NaAlO}_2$ ($1-x\text{NaPO}_3$) have been analyzed using solid state MAS NMR. The addition of aluminum to sodium phosphate glasses markedly changes their structure, thereby modifying both their chemical and physical properties.¹⁻⁴ Using ^{27}Al and ^{31}P MAS NMR, along with $^{31}\text{P}/^{27}\text{Al}$ and $^{31}\text{P}/^{23}\text{Na}$ TRAPDOR experiments, qualitative and quantitative information about the backbone and modifier structure as a function of mole percentage ^{27}Al and its coordination will be discussed. The Transfer of Populations in Dipolar Resonance, TRAPDOR, experiments^{5,6} allow for the detection of the dipolar coupling between, and therefore proximity of, ^{23}Na and ^{31}P . In this presentation, glasses are noted by their batch composition: e.g. a glass labeled 50-10-40 is batched (in mole%) as 50 Na₂O 10Al₂O₃ 40P₂O₅. We will classify the glass structures using a Q_n^m notation, where n is the number of P nearest neighbors (NNN) per P tetrahedron and m is the number of AlNNN per P tetrahedron.

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^{31}P NMR MAS Spectra

- The ^{31}P spectrum of the modifier-rich NaPO₃ base glass (50-0-50) is consistent with a structure having a linear chain of Q_2^0 groups terminated by Q_1^1 end groups. Results from a Radio-Frequency Dipolar Recoupling (RFDR) experiment done on this sample support this model.
- Addition of aluminum depolymerizes the glass network: replacing Na-O bonds with Al-O bonds and also some P-O bonds by Al-O bonds.⁷⁻⁹ In glass 50-2.5-47.5 the replacement of a P-O-P bond by a P-O-Al bond is responsible for the creation of the resonance at -6.92 ppm. These new Q_1^1 sites also decrease the shielding on the Q_2^0 sites (see ^{31}P Table 1).
- In NAP-4 (50-7.5-42.5) the Q_2^0 group has become so deshielded (-13.5 ppm) that it is no longer is resolvable as a separate peak. Rather, both it and the Q_1^1 resonance exist as shoulder features on the upfield and downfield sides of the Q_1^1 peak, respectively.

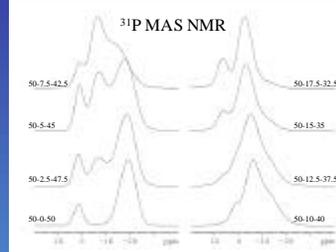


Table 1: ^{31}P NMR Data

Glass ID	NaPO ₃	AlPO ₃	Al ₂ O ₃	P ₂ O ₅	Al(4)	Al(5)	Al(6)	Al(7)
NAP-1	50-0-50	0	0	100	0	0	0	0
NAP-2	50-2.5-47.5	2.5	47.5	49.5	100	0	0	0
NAP-3	50-5-45	5	45	50	100	0	0	0
NAP-4	50-7.5-42.5	7.5	42.5	50	100	0	0	0
NAP-5	50-10-40	10	40	50	100	0	0	0
NAP-6	50-15-35	15	35	50	100	0	0	0
NAP-7	50-20-30	20	30	50	100	0	0	0
NAP-8	50-25-25	25	25	50	100	0	0	0
NAP-9	50-30-20	30	20	50	100	0	0	0
NAP-10	50-35-15	35	15	50	100	0	0	0
NAP-11	50-40-10	40	10	50	100	0	0	0
NAP-12	50-45-5	45	5	50	100	0	0	0
NAP-13	50-50-0	50	0	50	100	0	0	0

^{27}Al NMR MAS Spectra

- Depolymerization of the NaPO₃ glass network with addition of $\alpha\text{-Al}_2\text{O}_3$ results in a variety of aluminum coordinations.
- While six-coordinated aluminum, Al(6), dominates the ^{27}Al spectra through 10 mole% Al, all of the NAP glasses have some fraction of their aluminum content existing in Al(4), Al(5) and Al(6) environments.
- The preferred coordination of aluminum changes from Al(6) to Al(4) at 12.5 mole% Al, which coincides with changes to the ^{31}P chemical shifts of the various sites (see ^{31}P Table 1).
- The relative peak area (RA) of the Al(4) and Al(5) environments increase as the mole% Al increases (see ^{27}Al Table 2). The RA of Al(4) increases from 4% to nearly 75% along this compositional tie line, while the Al(5) RA levels off at ~20% in 50-10-40. The reduction to the RA of Al(6) is from 86% in (50-2.5-47.5) to 5% in (50-17.5-32.5).

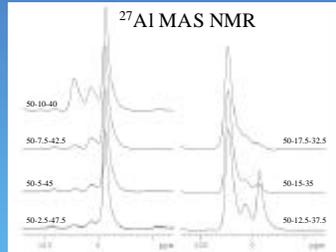
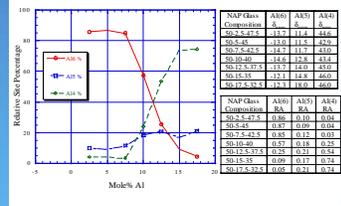
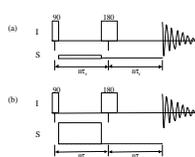


Table 2: Aluminum Coordination vs. Mole Percent Aluminum



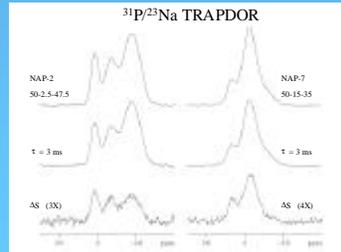
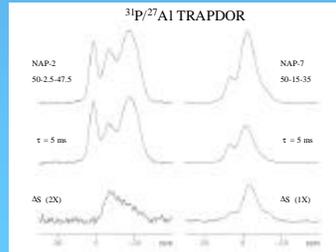
TRAPDOR Experiment

- The TRAPDOR pulse sequence is applied under MAS conditions during rotational period, τ_r . It consists of two parts: (a) a spin echo acquired without S-pulse decoupling (due to high attenuation on the Y amplifier), and (b) repeating the spin echo experiment with application of a 50 kHz rf pulse to the S nuclei.
- Imposition of the S-pulse causes a transfer-of-populations within a Zeeman states. This affects the evolution of the I spins that are dipolar coupled to them, thus providing proximity information.



TRAPDOR Results

- The dipolar deshielding effects of the TRAPDOR experiment were found to increase with increasing RF amplitude.
- $^{31}\text{P}/^{27}\text{Al}$ TRAPDOR experiments show: (a) In (50-2.5-47.5), aluminum coordinates preferentially to the ^{31}P resonance at -7.46 ppm, Q_1^1 , and to the Q_2^0 resonance; (b) no effects occur to the ^{31}P resonance at +1.74 ppm, Q_2^0 , in (50-2.5-47.5); (c) in NAP-7 all of the ^{31}P resonances are affected, but with preference to their upfield distribution; and (d) the resolution of the Q_2^0 environment in (50-15-35) is distinct in the TRAPDOR difference spectrum, ΔS .
- $^{31}\text{P}/^{23}\text{Na}$ TRAPDOR experiments show: (a) the ^{23}Na nuclei have dipolar coupling to all the ^{31}P resonances in the glasses studied; (b) in (50-2.5-47.5), ^{23}Na dipolar coupling is partial to the +1.74 and -7.46 ppm ^{31}P resonances; (c) the amount of dipolar coupling between ^{23}Na and ^{31}P in glass (50-15-35) increases as +6.3 ppm > -3.07 ppm > -12.25 ppm.



Conclusions

- Systematic changes in the structure of sodium phosphate glass by addition of alumina can be qualitatively and quantitatively analyzed using ^{31}P , ^{27}Al and ^{23}Na MAS NMR experiments.
- A transition point in the depolymerization of the NAP glasses studied appears between 10 and 12.5 mole% aluminum. In this region, the preferred coordination of aluminum changes from Al(6) to Al(4), and all the ^{31}P resonances, particularly the Q_2^0 environment, become less shielded.
- $^{31}\text{P}/^{23}\text{Na}$ and $^{31}\text{P}/^{27}\text{Al}$ TRAPDOR experiments use the dipolar coupling between the nuclei to show the proximity of ^{23}Na and ^{27}Al nuclei, respectively, with each of the ^{31}P environments.

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