

Synthesis of Aluminophosphate and Sodium Aluminophosphate Gels and Glasses

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Abstract

The gels and glasses of AlPO_4 and sodium aluminophosphate with composition of $40\text{Na}_2\text{O}-20\text{Al}_2\text{O}_3-40\text{P}_2\text{O}_5$ are prepared through a novel sol-gel route based on the reaction of aluminum lactate with H_3PO_4 and NaH_2PO_4 in aqueous solution. The sol-gel chemistry was characterized by high-resolution solution NMR and solid state ^{27}Al and ^{31}P MAS NMR, and $^{27}\text{Al}\{^{31}\text{P}\}$ Rotational Echo Double Resonance (REDOR) techniques. Detailed NMR data confirm that the local structures, the distributions of sites and the degree of Al/P connectivity in the sol-gel derived glasses are essentially indistinguishable with those of the melt-cooled glasses.

INTRODUCTION

Phosphate glasses are materials of technological interest due to higher thermal coefficient and lower transition temperatures than silicate and borate glasses [1,2]. The potentiality of these glasses is well recognized in applications as laser devices, sensors, solid-state batteries, and hermetic seals to high expansion metals, etc [3-6]. Technological applications of phosphates are limited due to their susceptibility to both aqueous and chemical attack. Strengthening of phosphate glasses is accomplished through the addition of aluminum into the network [7]. The sol-gel process has become a quite attractive technique, because of the possibility of producing very homogeneous multi-component oxide glasses at the temperatures much lower the melting temperature [8]. During the last decade considerable attention has focused on the use of sol-gel routes to aluminophosphate materials [9-13]. Since commonly used aluminum alkoxide precursors are highly reactive towards water, resulting in rapid hydrolysis and precipitation processes [14], the introduction of alumina into multiple-network former systems has remained a considerable challenge. Recently we reported a novel Al-precursor, aluminum lactate, which has been used, for the first time, in the preparation of alumina-based gels and glasses [15]. In this paper, we present a sol-gel synthesis of aluminophosphate and sodium aluminophosphate gels and glasses, based on the reaction of aluminum lactate with ortho-phosphoric acid and sodium dihydrogenphosphate in aqueous solution. Also, detailed liquid and solid state NMR experiments are reported to reveal the relevant species present in the precursor solutions, sols, gels and final glassy materials.

EXPERIMENTAL PROCEDURE

Preparation and Methods

AlPO_4 and sodium aluminophosphate with composition of $40\text{Na}_2\text{O}-20\text{Al}_2\text{O}_3-40\text{P}_2\text{O}_5$ were prepared via sol-gel route in aqueous solutions, using aluminum lactate (98%, Fluka), H_3PO_4 (1M) and NaH_2PO_4 (>99%, Aldrich) as precursors. H_3PO_4 (1M) solution was prepared by dissolving the solid ortho-phosphoric acid (>99%, Fluka) into distilled water. The pH of

precursor solutions was adjusted with freshly prepared chloride acid (1M, puriss. p.a., Fluka) or ammonia solution (1 M, diluted from conc. ammonia solution, Aldrich) and controlled within 0.01 units by a pH meter (WTW pH 320, Germany). In a typical preparation, 0.004 mol (~1.18g) aluminum lactate was added to 12 ml distilled water followed by addition of 4 ml H₃PO₄ (1M) solution or 0.008 mol NaH₂PO₄. After drying the clear resulting solution in the open air for several hours at 40~75 °C or several days at room temperature, transparent gel can be obtained. After heating the xerogels around 500°C for several hours, amorphous glasses were obtained. In order to eliminate entrapment of organics in the glass, the precursor gels need drying under vacuum ($p < 10^{-4}$ mbar) at 150-200°C for 12 h before increasing the temperature to 500 °C at a rate of 0.5 K per minute. Crystallinity was checked via x-ray powder diffraction using the Guinier method, with Cu K_{α1} radiation and -quartz ($a = 491.30$ pm, $c = 540.46$ pm) as an internal standard. Thermogravimetric analysis (TGA) were carried out on a NETZSCH STA409 instrument using a heating rate of 10 K/min.

For comparison with the sol-gel derived glasses, a bulk glass sample having the same composition (40 Na₂O · 20 Al₂O₃ · 40 P₂O₅) was prepared by the melt cooling route: a stoichiometric mixture of NaPO₃ and Al₂O₃ (Fluka) was heated at 1400 °C for 3 h in a Pt crucible within a Nabertherm Supertherm furnace (HFL16/17).

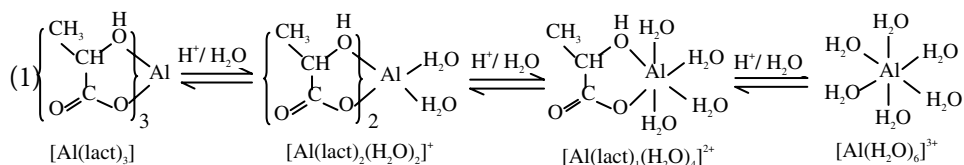
NMR Studies

All the NMR measurements were carried out at ambient temperature on Bruker DSX-400 and DSX-500 spectrometers, using 4 mm MAS-NMR probes. At the two fields strength of 9.4 and 11.7 T, the resonance frequencies were, respectively, 104.2 and 130.3 MHz for ²⁷Al, and 160.4 and 202.5 MHz for ³¹P. Liquid state NMR studies were conducted on stationary samples located inside zirconia rotors, whereas solid state NMR data were obtained at MAS rotation frequencies of 10 ± 2 kHz. Typical acquisition parameters were pulse length 5.0 μs - 90° (³¹P) and 1.0 μs - 30° (²⁷Al), recycle delay 60 s (³¹P) and 1 s (²⁷Al), number of scan 128 (³¹P) and 1024 (²⁷Al), respectively. The ²⁷Al and ³¹P NMR shift was referenced to 1 M Al(OH₂)₆³⁺ and 85% H₃PO₄, respectively.

To probe for ²⁷Al - ³¹P connectivities, the rotational echo double resonance (REDOR) technique [16-19] was used. This approach uses special double irradiation methods to introduce the heteronuclear dipole-dipole interactions between the ²⁷Al and the ³¹P nuclei - normally averaged out by MAS - back into the experiment. Specifically, the REDOR variant used in the present study records the rotor-synchronized ²⁷Al MAS NMR spin echos while applying 180° pulses to the ³¹P spins during the rotor period. For qualitative measurements, the ²⁷Al signal intensities (S and S_0) obtained in the presence and the absence of ³¹P irradiation were recorded. For more quantitative purposes whole REDOR curves ($S_0 - S$)/ S_0 were measured under systematic increment of the dipolar evolution time (NT_r = number of rotor cycles times rotor period). These experiments were carried out at two different spinning speeds per data set, using 90° pulse lengths of 3 s for both ²⁷Al (selective excitation conditions) and ³¹P. The compensated REDOR method described in reference [19] was used for correcting the effects of small pulse imperfections. Using our previously established methodology [18, 19] approximate dipolar second moments characterizing the magnitudes of these interactions were then obtained by detailed analysis of the REDOR curvatures in the limit of short dipolar evolution times ($0 \leq (S_0 - S)/S_0 \leq 0.2$).

RESULTS, ASSIGNMENT AND DISCUSSION

To gain insight into the solution \rightarrow gel \rightarrow glass transition, ^{27}Al and ^{31}P NMR experiments were recorded at the various processing steps. Figure 1 and 2 summarize the ^{27}Al and ^{31}P NMR spectra obtained after addition of 2 equivalents of NaH_2PO_4 into $\text{Al}(\text{lact})_3$ solution, as a function of pH. The ^{27}Al spectra of initial $\text{Al}(\text{lact})_3$ precursor solution are also shown in the upper of Figure 1. As shown in Figure 1a-d, in $\text{Al}(\text{lact})_3$ precursor solution there exists four species - $\text{Al}(\text{lact})_3$, $\text{Al}(\text{lact})_1(\text{H}_2\text{O})_4^{2+}$, $\text{Al}(\text{lact})_2(\text{H}_2\text{O})_2^+$ and $\text{Al}(\text{H}_2\text{O})_6^{3+}$ around 0, 7.5, 14, and 22 ppm, respectively, owing to the following hydrolysis process [15].



After addition of NaH_2PO_4 solutions, the ^{27}Al spectra shift toward more shielding, exhibiting severe peak overlap. Previous investigation on the solution of aluminum lactate and sodium polyphosphate indicated that there exists four series of compounds, $\text{Al}(\text{lact})_3$, $\text{Al}(\text{lact})_1(\text{H}_2\text{O})_4$, $\text{Al}(\text{lact})_2(\text{H}_2\text{O})_{2-y}(\text{PO}_3)_y^{(1-y)^+}$ ($0 < y < 2$), and $\text{Al}(\text{H}_2\text{O})_{4-y}(\text{PO}_3)_y^{(2-y)^+}$ ($0 < y < 6$), respectively, in $\text{Al-lact}/\text{NaPO}_3$ solution [15]. Although we have no clear evidences, it's conceivable that the similar compounds, $\text{Al}(\text{lact})_{3-x}(\text{H}_2\text{O})_{2x-y}(\text{H}_2\text{PO}_4)_y^{(x-y)^+}$, should also be formed in $\text{Al-lact}/\text{NaH}_2\text{PO}_4$ solution, as well as in $\text{Al-lact}/\text{H}_3\text{PO}_4$ solution, through the following hydrolysis and complex processes.



The ^{31}P spectra (Figure 2) are composed of four species around 0, -7, -12 and -17 ppm, respectively. We will designate the phosphorus species in aluminophosphate materials using a $Q^n(m\text{Al})$ notation [20-22], where n is the number of P next-nearest-neighbor (NNN) per P tetrahedron and m is the number of Al NNN per P. Note that this notation makes no distinction as to the species of aluminum. It's readily to assign 0 and -7 ppm to free orthophosphate (i.e. $Q^0(0\text{Al})$ species) and orthophosphate bound to one Al ion (i.e. $Q^0(1\text{Al})$ species), respectively. As for the signal at -12 ppm, we assign to $Q^0(2\text{Al})$ species although the chemical shift of $Q^1(1\text{Al})$ species, reported value of -13 to -15 ppm in aqueous solution [23], is also near -12 ppm. Likewise, the signal at -17 ppm is assigned to $Q^0(3\text{Al})$ species although $Q^1(2\text{Al})$ species is also in this range. If $Q^1(1\text{Al})$ and $Q^1(2\text{Al})$ species exist in $\text{Al-lact}/\text{NaH}_2\text{PO}_4$ sols, the concentration of these species should decrease when decreasing pH value, which is contradictory to Figure 2. It's also conceivable that P-O-P linkage is much more hard to form, compared with the formation of P-O-Al bond, in present acid-sols circumstance. Furthermore, such assignments are supported by the advanced solid state NMR of corresponding xerogels. $^{31}\text{P}\{^{27}\text{Al}\}$ rotational echo adiabatic passage double resonance (REAPDOR) experiment [24,25] independently confirms that four species present in aluminophosphate xerogel at 0, -7, -13 and -18 ppm are $Q^0(0\text{Al})$, $Q^0(1\text{Al})$, $Q^0(2\text{Al})$ and $Q^0(3\text{Al})$, respectively [26].

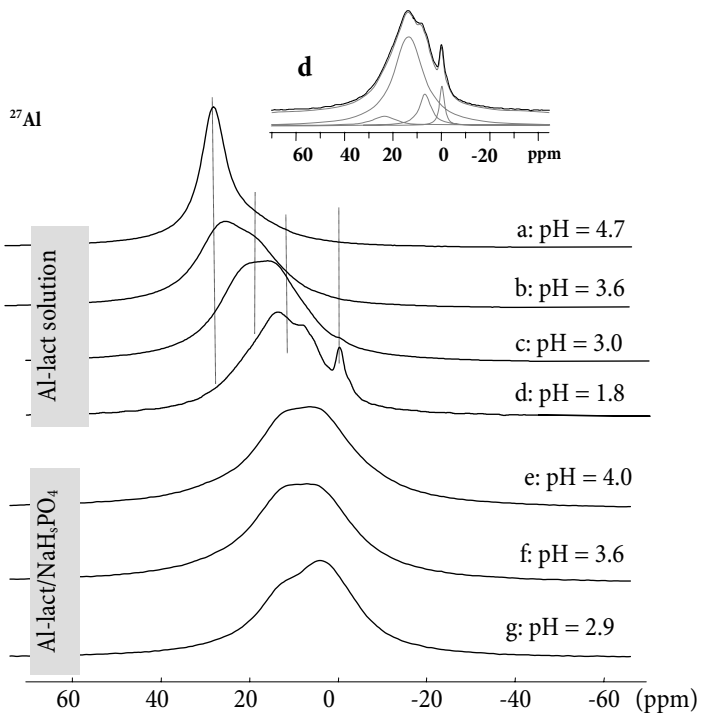


Figure 1: 130.3 MHz solution state ^{27}Al NMR spectra of Al-lact/ NaH_2PO_4 sols with $P/\text{Al} = 2$, as a function of pH value. The spectra of initial aluminum lactate solution are also shown in the upper of this figure, as a function of pH value. A typical spectral deconvolution for trace (d) is shown at the top.

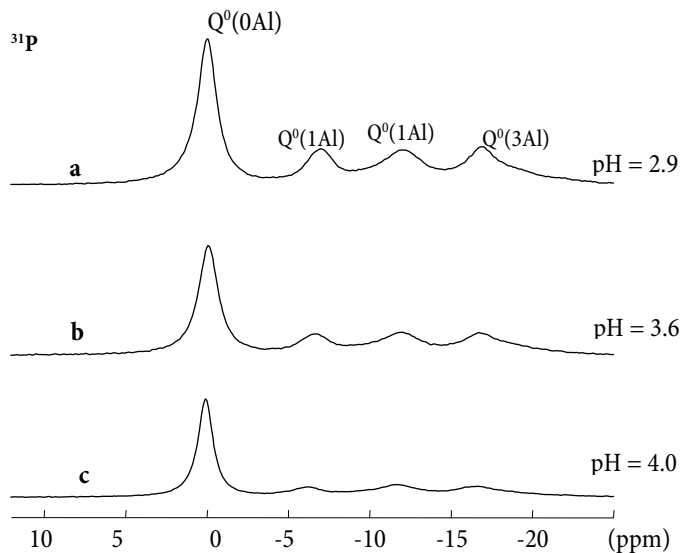


Figure 2: ^{31}P NMR (202.5 MHz) spectra of Al-lact/ NaH_2PO_4 sols with $P/\text{Al} = 2$, as a function of pH value

Clearly, increasing the concentration of H^+ tends the chemical equilibria of Eq.2 towards the right. Therefore, the concentrations of phosphorus species bound to Al ions, $Q^0(mAl)$ ($m=1\sim 3$), increase with raising the concentration of H^+ in solution, just as shown in Figure 2. The same trend is observed in Al-lact/ H_3PO_4 solutions (the spectra not shown here) when changing pH value of solution.

Gel and glass

Upon air-drying the sols, the transparent and colorless $AlPO_4$ and sodium aluminophosphate xerogels were obtained. Figure 3 shows the TGA traces of $AlPO_4$ xerogel (a) and $2Na_2O-Al_2O_3-2P_2O_5$ xerogel (b), indicating that volatile components (organics and water) are almost completely driven off below 350 °C. After heating the xerogels around 500°C for several hours, aluminophosphate glasses were obtained. The noncrystalline state of all samples was confirmed by the absence of any sharp X-ray power diffraction peaks.

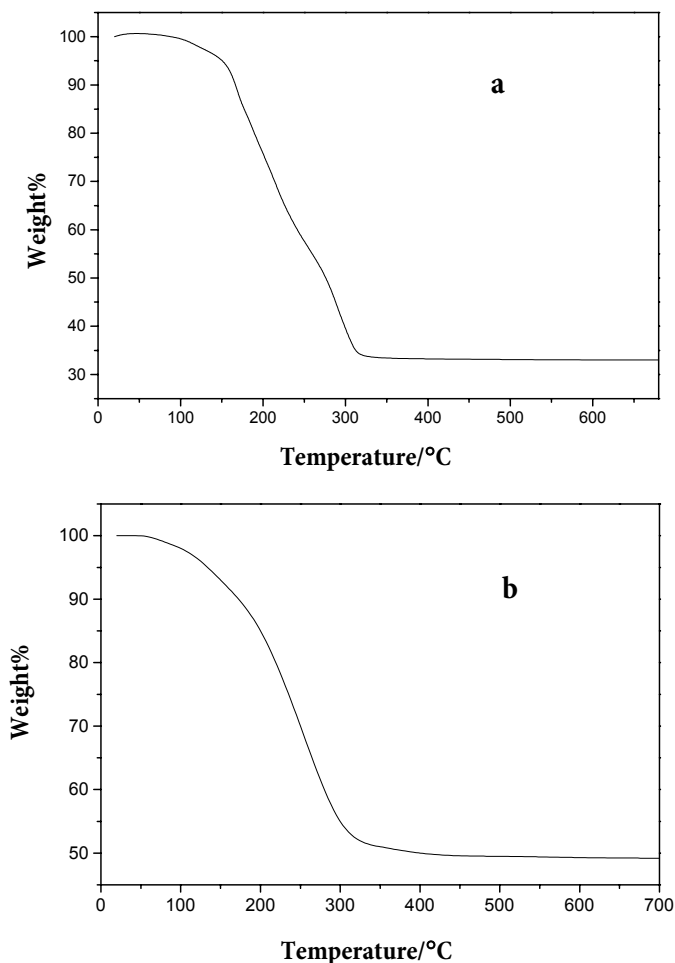


Figure 3: a) TGA traces of $AlPO_4$ xerogel formed at room temperature; b) TGA traces of $40Na_2O \cdot 20Al_2O_3 \cdot 40P_2O_5$ xerogel.

The ^{27}Al and ^{31}P MAS spectra of AlPO_4 xerogel and glass are shown in Figure 4. In ^{27}Al spectra of xerogel (see Figure 4 a), four signals are evident with peak maxima near 19, 5, -4, and -13 ppm. The $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR data reveal that the 19 ppm signal is hardly affected by ^{31}P irradiation, indicating that these ^{27}Al species are remote from phosphorus. Therefore the signal at 19 ppm is attributed to $[\text{Al}(\text{lact})_3]$ sites. In contrast, the signals of other components at 5, -4 ppm and -13 ppm are obviously reduced by ^{31}P irradiation in these experiments, indicating that some P are present in close proximity of these species. Figure 5 shows the $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR dephasing curves of these three components. We have analyzed the REDOR curvatures at short dipolar evolution times [18] in terms of site selective ^{27}Al - ^{31}P dipolar second moment values $M_2^{\text{P-Al}}$. The best fit values of the component at 5, -4, and -13 ppm, are 1.9, 3.8, and 6.1 KHz^2 , respectively, which are approximately equal to one third, two thirds and one, respectively, of that for $[\text{Al}(\text{OP})_6]$ site measured in the crystalline model compounds $\text{Al}(\text{PO}_3)_3$ [19]. Supposed the average Al-O-P next nearest neighbor distances are almost same in these species. We can conclude that the peaks at 5, -4 and -13 ppm are related to the species with two, four and six phosphorus neighbors, i.e. $[\text{Al}(\text{lact})_2(\text{OP})_2]$, $[\text{Al}(\text{lact})_1(\text{OP})_4]$ and $[\text{Al}(\text{OP})_6]$ sites, respectively. When gel annealed at 100 °C, a new Al site near 40 ppm occurs (Figure 4 b). This peak is well known in aluminophosphate materials and has been assign $\text{Al}(\text{OP})_4$ site [20-22]. After calcinations of 500 °C, Al(IV) species is overwhelming dominant in AlPO_4 glass (Figure 4 c), while the resonance related to Al(VI) species are negligible. At 600 °C, where the material is still amorphous by X-ray diffraction, both ^{27}Al and ^{31}P MAS spectra are completely same with those calcined at 500 °C.

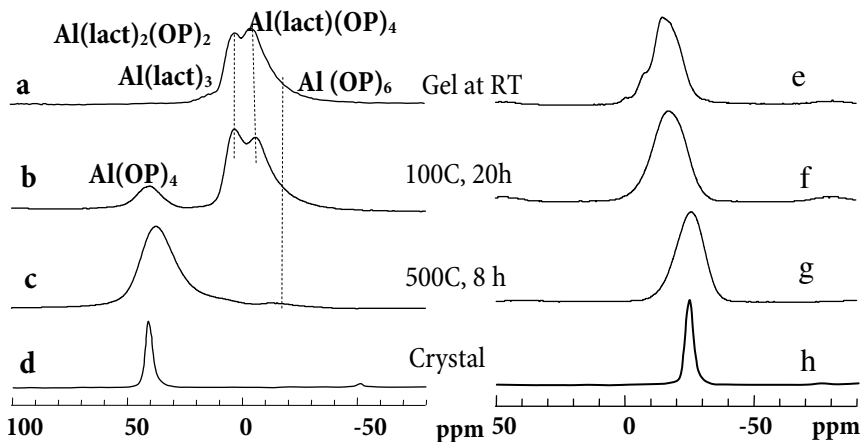


Figure 4: 104.2 MHz ^{27}Al (left) and 160.4 MHz ^{31}P (right) NMR spectra of AlPO_4 gel and glass. For comparison, the spectra of AlPO_4 crystal compound also show in the bottom.

From ^{31}P MAS spectra of AlPO_4 samples (Figure 4 e-f), one can clearly see that the shielding of phosphorus increases in the process from gel to glass, reflecting that the degree of P/Al connectivity increases in the conversion of gel to glass. In glass annealed at 500 °C, it appears all phosphorus are $\text{Q}^0(4\text{Al})$ circumstance - as expected from ^{27}Al MAS spectra (Figure 4 c), indicating that our gel-derived AlPO_4 glass has a three-dimensional structure composed of phosphate tetrahedral bonded to four tetrahedral Al, similarly as in crystal AlPO_4 . For comparison, the ^{27}Al and ^{31}P MAS spectra of crystal AlPO_4 are also shown in the bottom of Figure 4.

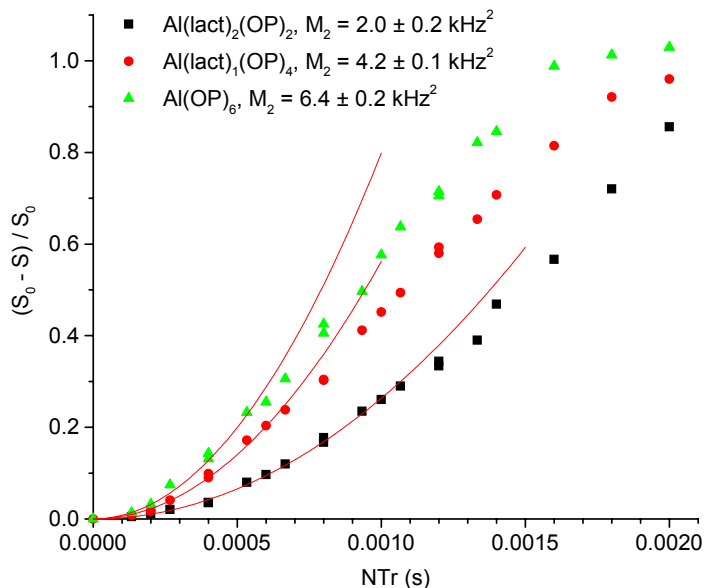


Figure 5: $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR-NMR of AlPO_4 xerogel. The different symbols denote the different aluminum coordination environments, for which site resolved REDOR curves can be measured. The parabolic curves symbolize the fits for the $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR data for the different Al sites, yielding the $M_2^{\text{P-Al}}$ values.

The ^{27}Al and ^{31}P MAS spectra of sol-gel derived sodium aluminophosphate glass, with composition of $40\text{Na}_2\text{O}-20\text{Al}_2\text{O}_3-40\text{P}_2\text{O}_5$, are shown in Figure 6. The ^{27}Al and ^{31}P MAS spectra of xerogel are similar with those of AlPO_4 xerogel and not shown here. After heating the gel sample at 500°C , the ^{27}Al spectrum shows three peaks near 45, 13 and -15 ppm. These peaks are also well known in melt-cooled sodium aluminophosphate glasses, and have been assigned to $[\text{Al}(\text{OP})_4]$, $[\text{Al}(\text{OP})_5]$ and $[\text{Al}(\text{OP})_6]$ sites respectively [20-22]. The ^{31}P NMR spectra can be deconvoluted into two separate contributions near -8 and -15 ppm. In conjunction with literature data [33,34], these resonances are most probably assignable to pyrophosphate (Q^1) species having one and two aluminum neighbors (i.e. $\text{Q}^1(1\text{Al})$ and $\text{Q}^1(2\text{Al})$). Both the ^{27}Al and the ^{31}P MAS-NMR spectra are virtually identical with those obtained on a sample prepared by conventional melt-cooling method (Figure 6a). Figure 6b illustrates further that the $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR results on both types of samples are essentially the same, revealing intimate Al-O-P connectivity for all the distinct Al(IV), Al(V), and Al(VI) coordination environments. The ^{27}Al - ^{31}P dipolar second moment values $M_2^{\text{Al-P}}$ for Al(IV), Al(V), and Al(VI) sites are 5.2 ± 0.2 , 5.9 ± 0.2 and 6.7 ± 0.2 kHz^2 , respectively, in sol-gel derived glass, which are 5.2 ± 0.2 (Al(IV)), 6.1 ± 0.2 (Al(V)) and 6.6 ± 0.2 (Al(VI)) kHz^2 , respectively, in melting glass. All of these results indicate convincingly that the local structures, the distributions of sites and the degree of Al/P connectivity in the sol-gel derived glasses and those of the melt-cooled glasses are essentially indistinguishable.

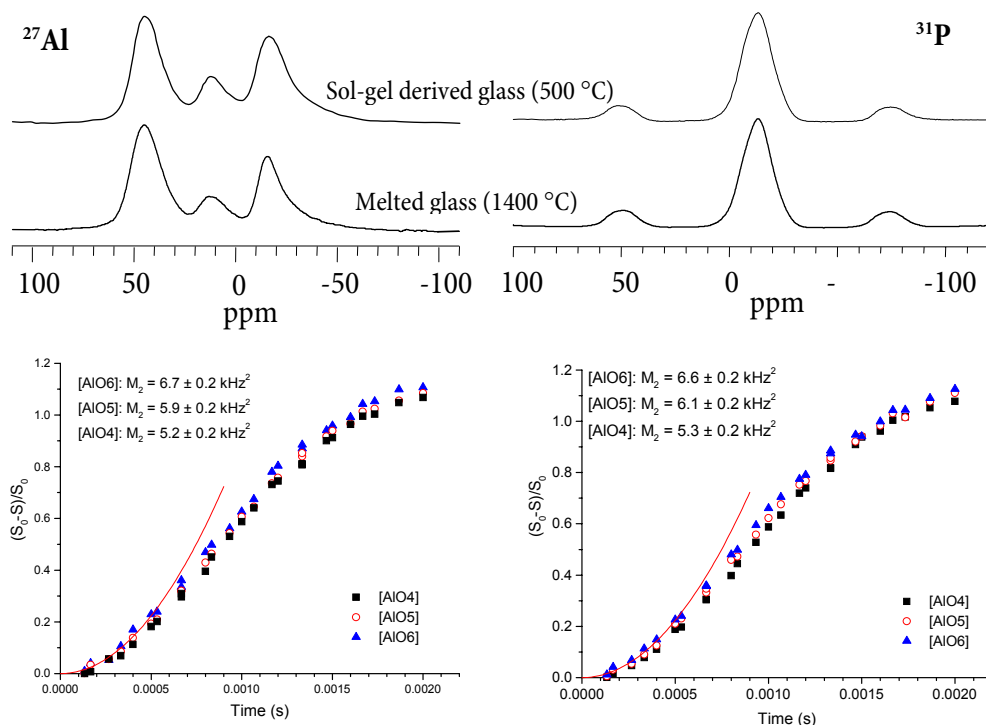


Figure 6: Spectroscopic comparison of the gel-derived glass with the melting glass:
 a) MAS NMR spectra of ^{27}Al (left) and ^{31}P (right). In each of the spectra the top trace depicts the glasses prepared from the sol-gel route, and the bottom trace depicts the glasses prepared via melt-cooling from 1400 °C.
 b) $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR-NMR. Sol-gel derived glass is shown on left, melt-cooled glasses on right. The parabolic curves symbolize the fits for the $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR data for the AlO_6 . Similar fits (not shown) were obtained for the REDOR data on the AlO_5 and AlO_4 sites

CONCLUSIONS

Overall, the gels and glasses of aluminophosphate and sodium aluminophosphate have prepared through a novel sol-gel route based on the reaction of aluminum lactate with H_3PO_4 and NaH_2PO_4 in aqueous solution. The sol-gel chemistry was characterized by high-resolution solution NMR and solid state MAS NMR, and $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR techniques. Detailed NMR results indicate that the structures of the gel-route and the molten-state route glasses are extremely closely related to each other.

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