

Phase identification and quantification in a devitrified glass using homo- and heteronuclear solid-state NMR

Grégory Tricot, Laurent Delevoye,* Gérard Palavit and Lionel Montagne

Received (in Cambridge, UK) 5th August 2005, Accepted 30th August 2005

First published as an Advance Article on the web 22nd September 2005

DOI: 10.1039/b511207a

A complex mixture resulting from the devitrification of an aluminophosphate glass has been studied for the first time using a combination of homo- and heteronuclear solid-state NMR sequences that offers the advantage of subsequent quantification.

Aluminophosphate based glasses have many important applications. They are used as biomaterials,¹ sealing glasses² and for radioactive waste confinement.³ These applications all have a close link with the devitrification process of phosphate glasses, which is the process that gives rise to the formation of crystallised compounds in a glassy matrix. A controlled crystallisation can lead to vitroceraamic materials with positive interesting properties (biomaterials). In some other cases, however, glass properties such as chemical durability and mechanical properties can be negatively and dramatically affected by the devitrification (sealing glasses, waste confinement). Thus, a good understanding of the crystallisation behaviour is necessary, which includes the determination of both the thermal range for which crystallisation occurs, and the nature of the formed phases. The determination of the nature of the crystallised compounds is generally achieved through X-ray diffraction (XRD). However, the efficiency of XRD is often tempered with both the formation of a large number of phases with low crystallinity, and a possible remaining amorphous part. On the other hand, NMR that probes the local environment of a nucleus, is not limited by the presence of amorphous parts and also by the low crystallinity of the compounds. Moreover, recent developments in solid-state NMR have provided a large set of pulse sequences that have proven to be successful in obtaining structural information on solids. For example, two-dimensional (2D) correlation experiments are now commonly used to study the ³¹P network of inorganic materials. In parallel, the problem of the additional second-order broadening, which remains on MAS spectra of quadrupolar nuclei has been overcome with the introduction of the 2D MQMAS experiment.⁴ In this communication, we will show that the combination of high-resolution homo- and heteronuclear NMR sequences enables the characterization of the phases present in a complex mixture of crystalline phosphates.

Hartmann *et al.* have investigated complex mixtures of phosphate phases using ³¹P MAS NMR associated with homonuclear 2D NMR experiments such as exchange NMR⁵ and 2D Radio Frequency Driven Recoupling (RFDR)⁵ correlation experiments.^{1,6} Both 2D NMR experiments are designed to show

cross-peaks between phosphorus sites that are spatially close and thus, that belong to the same crystallographic phase. In a polycrystalline silicon phosphate sample,⁶ Hartmann *et al.* separated the resonances from seven different phosphate structures contained within the mixture. The degree of condensation Q^n (n represents the number of neighbouring phosphate groups) for each phosphorus site was then determined through the ³¹P chemical shift tensors. Hartmann *et al.* also studied the structure of devitrified sodium and calcium aluminophosphate glasses.¹ The 2D RFDR spectrum revealed after devitrification the presence of at least four different phosphate compounds. As this study was only based on homonuclear sequences, the discrimination of the phosphate or aluminophosphate nature of the network was not possible. Hence, it is essential to probe the ³¹P/²⁷Al spatial proximity using *heteronuclear* NMR pulse sequences. This is especially important in order to determine whether the formed compounds are constituted with phosphate and/or aluminophosphate networks.

In this communication, we propose a solid-state NMR study of an aluminophosphate system using both the recently developed *homonuclear* ³¹P and *heteronuclear* ³¹P/²⁷Al NMR pulse sequences. This general approach will be illustrated through the study of a devitrified sodium aluminophosphate glass (41 Na₂O–20.5 Al₂O₃–38.5 P₂O₅) that has been proposed as a host matrix for radioactive waste.³ The aim is to reveal that Na₇(AlP₂O₇)₄PO₄ is the main phase resulting from the devitrification process of the glass.

The glass was prepared with appropriate quantities of reagent grade NaPO₃, Al(OH)₃ and Na₂CO₃. The starting mixture was ground thoroughly and heated slowly to 600 °C (1 °C min⁻¹) in order to remove CO₂ and H₂O. After mixing, the batch was melted at 1300 °C for 20 min and then, quenched between two steel plates. Thermal analysis indicated a glass transition temperature (T_g) at 412 °C and two crystallisation temperatures (T_c) at 506 and 613 °C, which are in good agreement with those reported by Donald *et al.*³ Finally, a thermal treatment was applied at 613 °C for 6 h in order to obtain the crystallisation of the glassy matrix.

³¹P and ²⁷Al NMR spectra (Fig. 1) of the glass and of the devitrified sample were recorded on a 400 MHz (9.4 T) Bruker spectrometer. The ³¹P and ²⁷Al MAS spectra (Fig. 1(a) and (d)) show characteristic broad resonances due to the distribution of bond lengths and angles within the glass. The ³¹P spectrum acquired after devitrification (Fig. 1(b)) shows narrow resonances that suggest the presence of several crystalline phases. Unfortunately, a complete assignment of the different resonances using ³¹P chemical shift was difficult due to the presence of phases that have probably never been studied before through solid-state NMR. The overlap of several peaks also prevented the use of spinning sidebands for the identification of Q^n sites through the

Laboratoire de Cristalochimie et Physicochimie du Solide, UMR-CNRS 8012, Ecole Nationale Supérieure de Chimie de Lille, Université des Sciences et Technologies de Lille, BP90108, 59655 Villeneuve d'Ascq, France. E-mail: laurent.delevoye@ensc-lille.fr

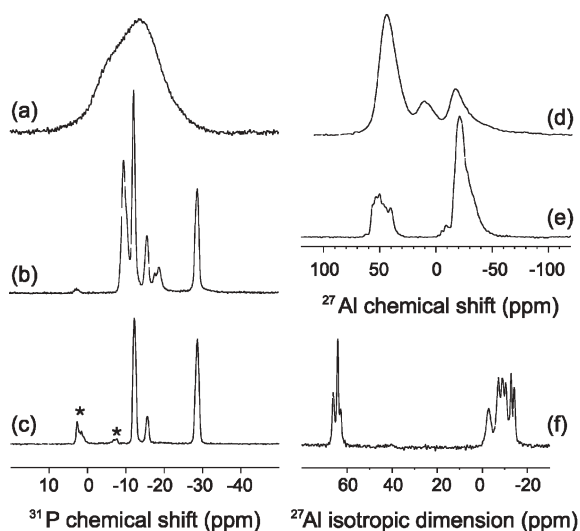


Fig. 1 ^{31}P MAS spectra of the 41 Na_2O –20.5 Al_2O_3 –38.5 P_2O_5 glass (a), after devitrification (b) and $\text{Na}_7(\text{AlP}_2\text{O}_7)_4\text{PO}_4$ phase (c) (*: impurity) acquired at a rotor spinning speed of 12 kHz, a $\pi/8$ pulse angle and a recycling delay of 20 s (a) and 120 s (b, c). ^{27}Al MAS spectra of the glass (d) and after devitrification (e) acquired at a rotor spinning speed of 12 kHz, a $\pi/10$ pulse angle and a recycling delay of 2 s. ^{27}Al 3Q-MAS isotropic projection of the devitrified sample (f). The 3QMAS experiment was acquired at an MAS speed of 20 kHz using the Z-filter pulse sequence composed of two hard pulses of 3.5 and 1.25 μs for 3Q excitation and reconversion, followed by a soft pulse of 9 μs . The 1024 \times 256 data points were collected with rotor synchronisation in the t_1 dimension and using the STATES 2D acquisition method. Each transient was accumulated with 240 scans.

analysis of the chemical shift anisotropy (CSA) parameters. The ^{27}Al spectrum of the glass (Fig. 1(d)) exhibits the three aluminium resonances usually found in phosphate glasses: AlO_4 (40 ppm), AlO_5 (0 ppm) and AlO_6 (–30 ppm). After devitrification (Fig. 1(e)), broad featureless ^{27}Al resonances are located in the tetra- and octahedral regions. The isotropic projection of the high-resolution 3QMAS spectrum is depicted in Fig. 1(f), showing that the mixture is composed of a large number of aluminium sites.

In a second step, we studied the phosphate network using 2D NMR experiments that enable the characterization of the correlations through both *space* (dipolar) and *bonds* (scalar). First, a RFDR sequence was used to highlight spatial proximity between the different ^{31}P sites. By assuming that ^{31}P nuclei which are close neighbours belong to the same phase, RFDR results provided information not only on the number of different phosphate compounds present in the sample but also on the number of crystallographic phosphorus sites present in each structure. In a RFDR spectrum, the absence of correlation between two phosphorus sites indicates that they do not belong to the same phase. The cross peak analysis (Fig. 2(a)) gave us the means to extract at least four different phosphate phases from the mixture. Among them, we will here focus on the three most intense ^{31}P sites at –12.3, –15.7 and –28.8 ppm, which will be referred to hereafter as P(1), P(2) and P(3), respectively. Cross-correlation resonances are significant, which indicate that these three phosphate sites belong to the same phase.

Second, the ^{31}P network was studied using the refocused INADEQUATE experiment⁷ in order to probe ^{31}P through *bond*

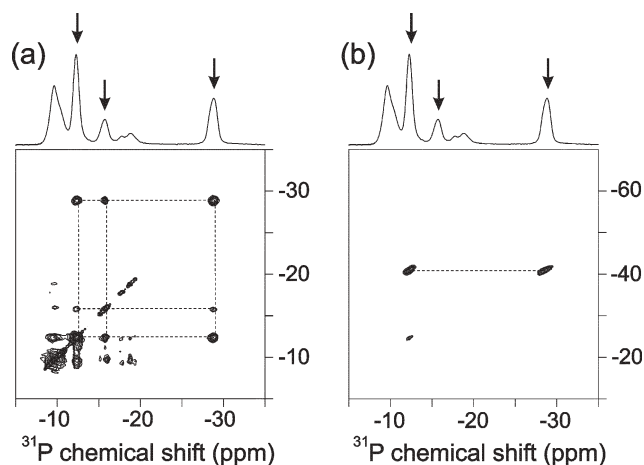


Fig. 2 RFDR (a) and refocused INADEQUATE (b) spectra of the devitrified sample at 9.4 T. The RFDR spectrum was acquired at a MAS speed of 10 kHz, using a mixing time of 10 ms and a recycling delay of 25 s. The 1024 \times 512 data points were collected with rotor synchronized in t_1 dimension and using the TPPI method. Each transient was accumulated with 16 scans. The refocused INADEQUATE spectrum was obtained at a MAS speed of 28 kHz. The excitation and reconversion periods were set to 6 ms. 256 t_1 increments (STATES method) with 16 transients each were collected. The recycling delay was set to 25 s.

correlations. This 2D sequence leads to off-diagonal correlation peaks between phosphorus sites that are involved in the formation of a P–O–P bond. The INADEQUATE spectrum of the devitrified glass is plotted in Fig. 2(b). We observe correlation-peaks between P(1) and P(3), which indicate that the crystallographic structure contains P(1)–O–P(3) species. Due to their chemical shift values, P(1) and P(3) sites are most probably Q^1 sites even though a Q^2 site can not be ruled out. On the other hand, P(2) is not connected through a chemical bond to either P(1) or P(3). Thus, P(2) is definitely an isolated Q^0 site, *i.e.* PO_4^{3-} (orthophosphate). Note here that the presence of auto-correlation resonances on the diagonal is not a sign for P(1)/P(1) or P(3)/P(3) auto-correlation through an oxygen bonding (P–O–P). As recently shown by Fayon *et al.*,⁸ their presence is due to cross terms between homonuclear dipole–dipole and chemical shift anisotropy interactions, and could be removed by increasing the MAS frequency, when possible.

$^{31}\text{P}/^{27}\text{Al}$ heteronuclear correlations were then studied in order to determine the aluminium to phosphorus connectivity of the P(1), P(2) and P(3) sites. More specifically, we wanted to know whether the devitrification resulted in the formation of phosphate or of aluminophosphate networks. The MQ-D-HETCOR sequence uses a transfer of magnetisation—so called cross polarisation (CP)—from the ^{27}Al to the ^{31}P in order to probe the spatial proximity of the two nuclei. Through a multiple-quantum excitation of the quadrupolar nucleus prior to CP, this experiment provides a hetero-correlation spectrum with a well-resolved ^{27}Al dimension.⁹ Nevertheless, the transfer is very sensitive to the aluminium offset, due to the quadrupolar nature of ^{27}Al nucleus such that the excitation of both tetra- and octahedral aluminium regions is not possible within the same spectrum. Hence, two MQ-D-HETCOR spectra are presented in Fig. 3(a) and (b) for the tetrahedral and the octahedral ^{27}Al regions, respectively. Note that the 2D spectra are shown with the 1D ^{31}P MAS spectrum (horizontal spectra) and

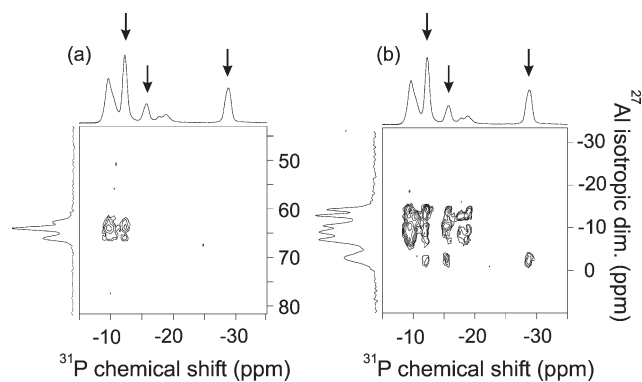


Fig. 3 $^{27}\text{Al}/^{31}\text{P}$ MQ-D-HETCOR spectra of the devitrified sample in the tetrahedral (a) and the octahedral (b) aluminium regions. The CP transfer was performed at ^{27}Al and ^{31}P RF fields of 7 kHz and 9 kHz, respectively. The contact time was set to 3.5 ms. The parameters for the 3QMAS part of the sequence are identical to those reported for Fig. 1(f). Both spectra were acquired with 128 t_1 increments and 480 transients each. The recycling delay was 2 s and the MAS speed was 12 kHz.

the isotropic projection of MQMAS ^{27}Al spectrum (vertical spectra) rather than with their traditional projections. Indeed, with our representation, ^{27}Al (or ^{31}P) that are not surrounded by at least one ^{31}P (or ^{27}Al) are not shown on the 2D mapping and would directly be assigned on the 1D spectra. This would indicate the presence of a purely aluminate (or purely phosphate) phase.

A large number of correlation peaks between the phosphorus and the aluminium sites can be observed in Fig. 3. This confirms that our sample is formed by a very complex mixture of crystalline phosphates. Furthermore, these spectra reveal that each phosphorus resonance is correlated with at least one ^{27}Al site, and *vice versa* (all the ^{27}Al resonances are correlated with at least one ^{31}P site). Consequently, it is possible to conclude that our devitrified glass is constituted of a complex mixture of aluminophosphate phases rather than of a phosphate or aluminate phase. This information is very important for the characterization of the chemical durability of the material. In particular, Fig. 3(b) shows that the three phosphorus sites, P(1), P(2) and P(3) are correlated with the same octahedral aluminium site (-4 ppm). It is important to mention that P(1) and P(2) which are correlated to a unique octahedral aluminium site are located at chemical shifts very close to other resonances. These resonances are related to other phases, the determination of which is beyond the scope of this communication.

Finally, ^{31}P network analysis indicated the presence in our mixture of a phosphate structure that contains three phosphorus sites, of which two are chemically linked through P–O–P bonds. The study of the $^{27}\text{Al}/^{31}\text{P}$ correlations indicate that this phase has in fact an aluminophosphate network with a unique octahedral aluminium site.

The structural analysis performed on our 2D NMR spectra can now be compared with the information available in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5$ crystallographic database (see Table 1). For each compound, we listed the number of ^{31}P sites, their degree of condensation and the number of aluminium sites present in the structure. This gave us the means to extract a single phosphate phase $\text{Na}_7(\text{AlP}_2\text{O}_7)_4\text{PO}_4^{10}$ for which the structure is in full agreement with our NMR data. The $\text{Na}_7(\text{AlP}_2\text{O}_7)_4\text{PO}_4$ structure

Table 1 Structural database of the crystalline phases in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5$ system including the number of phosphorus crystallographic sites, their degree of condensation (Q^n) and the number and coordination of aluminium sites.

	^{31}P	Q^n	^{27}Al
NaAlP_2O_7	2 Sites	Q^1	1 Octahedral site
$\text{Na}_3\text{Al}_2(\text{PO}_4)_3$	3 Sites	Q^0	1 Tetrahedral site
$\text{Na}_7(\text{AlP}_2\text{O}_7)_4\text{PO}_4$	3 Sites	$2Q^1/Q^0$	1 Octahedral site
$\text{Na}_3\text{AlP}_3\text{O}_{23}$	2 Sites	Q^2/Q^3	1 Octahedral site
$\text{Na}_{3-3x}\text{Al}_x\text{PO}_4$	3 Sites	Q^0	3 Tetrahedral sites
$\text{Al}(\text{PO}_3)_3$ [A]	1 Site	Q^2	1 Octahedral site
$\text{Al}(\text{PO}_3)_3$ [B]	3 Sites	Q^2	1 Octahedral site
$\text{Na}_5\text{P}_3\text{O}_{10}$	3 Sites	$2Q^1/Q^2$	—
$\text{Na}_4\text{P}_2\text{O}_7$	2 Sites	Q^1	—

is indeed composed of three different crystallographic phosphorus sites as indicated by the RFDR results, the phosphate network is made of one isolated site Q^0 (PO_4^{3-}) and two Q^1 sites ($\text{P}_2\text{O}_7^{4-}$) as deduced from the INADEQUATE spectrum. It is also constituted of an aluminophosphate network as we determined through the analysis of the $^{27}\text{Al}/^{31}\text{P}$ heteronuclear correlation spectrum. Because of the close similarity between those structural data and our NMR results, we can conclude that $\text{Na}_7(\text{AlP}_2\text{O}_7)_4\text{PO}_4$ is the main phase that is present in our phosphate based mixture. In a final step, we synthesized the phase in order to confirm our ^{31}P assignment (see Fig. 1(c)).

Another advantage for NMR is the easy access to quantitative measurements provided that the spectra have been recorded with a recycling delay which allows full relaxation between two acquisitions, and that the quantification takes into account all spinning sidebands. In our study, the ^{31}P resonance at -28.8 ppm was taken as the reference intensity for the quantification of $\text{Na}_7(\text{AlP}_2\text{O}_7)_4\text{PO}_4$ in the devitrified glass. Indeed, the hetero-correlation MQ-D-HETCOR spectrum in Fig. 3(a) and (b) shows that there is no resonance at -28.8 ppm that belongs to another formed phase. By keeping close watch of these parameters, we were further able to determine that more than 40% of the total phosphorus of the mixture is present in $\text{Na}_7(\text{AlP}_2\text{O}_7)_4\text{PO}_4$ phase.

We have here shown that a complex devitrified aluminophosphate sample can be analysed through the combination of homo- and heteronuclear NMR analyses. Broadly speaking, our approach can be applied to other types of materials, including devitrified glass of borophosphate and vanadophosphate systems.

Notes and references

- P. Hartmann, J. Vogel, U. Friedrich and C. Jäger, *J. Non-Cryst. Solids*, 2000, **263&264**, 94.
- R. K. Brow and D. R. Tallant, *J. Non-Cryst. Solids*, 1997, **222**, 396.
- I. W. Donald and B. L. Metcalfe, *J. Non-Cryst. Solids*, 2004, **348**, 118.
- L. Frydman and J. S. Harwood, *J. Am. Chem. Soc.*, 1995, **117**, 19, 5367.
- A. E. Bennett, J. H. Ok, R. G. Griffin and S. Vega, *J. Chem. Phys.*, 1992, **96**, 8264.
- P. Hartmann, C. Jana, J. Vogel and C. Jäger, *J. Non-Cryst. Solids*, 1996, **258**, 107.
- F. Fayon, G. Le Saout, L. Emsley and D. Massiot, *Chem. Commun.*, 2002, **16**, 1702.
- F. Fayon, D. Massiot, M. H. Levitt, J. J. Titman, D. H. Gregory, L. Duma, L. Emsley and S. P. Brown, *J. Chem. Phys.*, 2005, **122**, 194313.
- C. Fernandez, C. Morais, J. Rocha and M. Pruski, *Solid State Nucl. Magn. Reson.*, 2002, **21**, 61.
- M. de la Rochere, A. Kahn, F. d'Yvoire and E. Bretey, *Mater. Res. Bull.*, 1985, **20**, 27.