

An advanced NMR protocol for the structural characterization of aluminophosphate glasses

Leo van Wüllen*, Grégory Tricot, Sebastian Wegner

Institut für Physikalische Chemie, Westfälische Wilhelms-Universität Münster, Correnstrasse 30-36, 48149 Münster, Germany

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Abstract

In this work a combination of complementary advanced solid-state nuclear magnetic resonance (NMR) strategies is employed to analyse the network organization in aluminophosphate glasses to an unprecedented level of detailed insight. The combined results from MAS, MQMAS and $^{31}\text{P}\{-^{27}\text{Al}\}$ -CP-heteronuclear correlation spectroscopy (HETCOR) NMR experiments allow for a detailed speciation of the different phosphate and aluminate species present in the glass. The interconnection of these local building units to an extended three-dimensional network is explored employing heteronuclear dipolar and scalar NMR approaches to quantify P–O–Al connectivity by $^{31}\text{P}\{^{27}\text{Al}\}$ -heteronuclear multiple quantum coherence (HMQC), -rotational echo adiabatic passage double resonance (REAPDOR) and -HETCOR NMR as well as $^{27}\text{Al}\{^{31}\text{P}\}$ -rotational echo double resonance (REDOR) NMR experiments, complemented by ^{31}P -2D-J-RESolved MAS NMR experiments to probe P–O–P connectivity utilizing the through bond scalar J-coupling.

The combination of the results from the various NMR approaches enables us to not only quantify the phosphate units present in the glass but also to identify their respective structural environments within the three-dimensional network on a medium length scale employing a modified Q notation, Q^n_{m,AlO_x} , where n denotes the number of connected tetrahedral phosphate, m gives the number of aluminate species connected to a central phosphate unit and x specifies the nature of the bonded aluminate species (i.e. 4, 5 or 6 coordinate aluminium).

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1. Introduction

Phosphate-based glasses represent a technologically important class of materials with a wide range of applications including biomaterials [1], sealing glasses [2], fast ion conductors as well as laser hosts [3]. All these applications benefit from the low glass transition temperature (T_g) values or from the high thermal expansion coefficient of the phosphate network. The poor chemical durability of pure phosphate glasses severely restricts their straightforward application in the various technological fields. However, this drawback can be overcome by adding co-oxides to the glass batches. The addition of Al_2O_3 , e.g., has been shown to considerably increase the chemical durability of the phosphate-based glasses [4,5], especially

improving the resistance against moisture attack. The incorporation of alumina to the phosphate glasses is supposed to induce some cross-linking between the phosphate chains via the formation of Al–O–P linkages, hence increasing the stiffness of the glass network. These aluminophosphate glasses find application as anti-oxidation coatings or as confining matrices for nuclear waste materials.

During the last decade, a wealth of studies has been devoted to the elucidation of the structural changes upon addition of Al_2O_3 in these glasses. Among the various structural probes available, especially solid-state nuclear magnetic resonance (NMR) spectroscopy has contributed to the understanding of the glass structure. However, to date, no concise structural model of the network organization in these glasses is available. While the determination of the local structure of the aluminate species present in the glasses proves straightforward and the results—with

*Corresponding author. Fax: +49 251 8329159.

E-mail address: wullen@uni-muenster.de (L. van Wüllen).

octahedral AlO_6 species dominating at low alumina content and tetrahedral AlO_4 units at high alumina content—seems more or less undisputed, a concise phosphate speciation in these glasses is severely complicated due to several reasons. First, in a mixed aluminophosphate network, apart from the pure phosphate species Q_0^1 and Q_0^2 a variety of Q_m^n units [6] may exist leading to strongly overlapping signals in the ^{31}P -MAS NMR spectrum that are impossible to deconvolute without any additional information. Second, the usual protocol of taking a chemical shift reference base from crystalline model compounds to aid in the assignment of resonance lines proves to be of only limited applicability in the case of aluminophosphate species, since only some of the possible Q_m^n units occur in crystalline compounds, e.g. Q_3^1 (NaAlP_2O_7) [7,8] or Q_x^0 ($x = 1, 2, 3$ and 4) ($\text{Na}_{3-3x}\text{Al}_x\text{PO}_4$) [9]. Thus, the chemical shift assignments of some of the possible phosphate species have to be based on assumptions. Unluckily, and that is third, the chemical shift evolution with increasing alumina content is governed by two opposing effects: (a) a decrease in the phosphorous condensation degree ($Q^2 \rightarrow Q^1 \rightarrow Q^0$) which entails a deshielding and (b) an increase in the number of aluminate polyhedra connected to a central phosphate tetrahedron (m in the Q_m^n notation) which induces a shielding. As a further complication, the nature of the aluminate polyhedron connected to the central phosphate tetrahedron has a distinct influence on its chemical shift. For example, a phosphorous in a Q_4^0 environment only surrounded by tetrahedral aluminium (as in the AlPO_4 structure) has a chemical shift of -25 ppm but this value shifts to -16 ppm for a Q_4^0 surrounded by octahedral aluminium ($\text{Na}_7(\text{AlP}_2\text{O}_7)_4\text{PO}_4$) [10,11].

Principally, the evaluation of structural motifs on medium length scales employing the heteronuclear dipolar coupling using two-dimensional heteronuclear correlation spectroscopy (2D HETCOR) or rotational echo double resonance (REDOR) spectroscopy (or the derivatives thereof) allows for a more rigorous assignment of the Q_m^n units present in the glass. Egan et al. [12] employed $^{31}\text{P}\{^{27}\text{Al}\}$ -2D-CP-HETCOR NMR experiments on sodium metaphosphate glasses $50\text{Na}_2\text{O}-x\text{Al}_2\text{O}_3-(50-x)\text{P}_2\text{O}_5$ ($2.5 < x < 20$) to improve the spectral resolution of the different phosphate sites present in the glass. The comparison between ^{31}P MAS NMR spectra and the one dimensional slices taken from the 2D CP-HETCOR spectra in combination with a chemical shift reference base of crystalline model compounds led these authors to determine the presence of Q_1^0 , Q_3^0 and Q_2^1 moieties in the glass matrix. However, the important information about the number of connected aluminate species to a given phosphate tetrahedron (m in the Q_m^n notation) is not obtainable from these experiments.

Lang et al. [13] performed $^{31}\text{P}\{^{27}\text{Al}\}$ and $^{31}\text{P}\{^{23}\text{Na}\}$ transfer of population in double resonance (TRAPDOR) NMR experiments to probe the medium range order in the aluminophosphate network. They deduced the presence of

Q_0^2 and Q_1^1 at low Al_2O_3 content and Q_2^1 as well as Q_1^0 and Q_2^0 for higher Al_2O_3 contents. Unfortunately, TRAPDOR experiments are not sensitive to aluminium coordination and a quantitative analysis was not attempted.

The same glasses were obtained via the sol-gel route by Zhang et al. [14]. Here, the analysis of $^{27}\text{Al}\{^{31}\text{P}\}$ -REDOR NMR experiments led to an unambiguous determination of $\text{Al}(\text{OP})_6$ and $\text{Al}(\text{OP})_4$ moieties for octahedral and tetrahedral aluminate species present in the sol gel glasses.

All together, while highlighting specific areas of the glass structure on short and intermediate length scales, the work published so far only provides partial information about the network organization and does not allow for a detailed glass model.

In the present paper we present a reinvestigation of the structure of aluminophosphate-based glasses employing a combination of complementary advanced solid-state NMR strategies.

Glasses in the system $50\text{K}_2\text{O}-x\text{Al}_2\text{O}_3-(50-x)\text{P}_2\text{O}_5$ ($2.5 < x < 20$) were investigated. Since the emphasis of this contribution is on the description of the solid-state NMR protocol which is employed to obtain an as complete description as possible of the glass structure, the strategy is illustrated with the help of the results for a single glass composition, $50\text{K}_2\text{O}-10\text{Al}_2\text{O}_3-40\text{P}_2\text{O}_5$. The results for the complete glass series together with a more detailed description of the glass model (as a function of the alumina content) is presented elsewhere. While MAS, MQMAS, $^{27}\text{Al}\{^{31}\text{P}\}$ -CP-HETCOR and $^{31}\text{P}\{^{27}\text{Al}\}$ -HMQC NMR experiments allow for a detailed speciation of the different phosphate and aluminate species present in the glass, the interconnection of these local building units to an extended three-dimensional network is explored employing heteronuclear NMR approaches to quantify P–O–Al connectivity by $^{31}\text{P}\{^{27}\text{Al}\}$ -REAPDOR and -HETCOR NMR as well as $^{27}\text{Al}\{^{31}\text{P}\}$ -REDOR NMR experiments, complemented by ^{31}P -2D-J-RESolved MAS NMR experiments to probe P–O–P connectivity employing through bond scalar J coupling. The glass structure as deduced from the results is discussed employing a modified Q notation, Q_{m,AlO_x}^n , where x denotes the nature of the connected Al-polyhedron, i.e. AlO_4 , AlO_5 or AlO_6 .

2. Experimental procedures

The $50\text{K}_2\text{O}-10\text{Al}_2\text{O}_3-40\text{P}_2\text{O}_5$ glass was prepared using the standard melt quenching technique. A first thermal treatment to 600°C ($1^\circ/\text{min}$) was applied to a mixture of reagent grade K_2CO_3 , $\text{Al}(\text{OH})_3$ and $(\text{NH}_4)_2\text{HPO}_4$ in a Pt crucible to remove H_2O , NH_3 and CO_2 . The batch was then heated for 20 min at 1000°C before being quenched between two copper plates. The obtained glass was transparent and colourless; the amorphicity was confirmed by X-ray diffraction (XRD). Since the weight loss proved to be less than 2%, we use the batch composition to give the glass composition.

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