THE NMR INFORMATION ON PHOSPHATE GLASSES: A REVIEW

PIERCARLO MUSTARELLI

Department of Physical Chemistry and INFM
University of Pavia, Via Taramelli 16, 27100 Pavia, Italy

Abstract Phosphate glasses are of technological interest for electrochemical devices, as bioactive materials, and also for the electronic industry. Solid-state NMR, chiefly coupled with magic angle sample spinning (MAS), is a valuable technique to obtain information on short-range order and connectivity in phosphate glasses. In this paper the most recent advances in the field will be reviewed, and more emphasis will be given to solid-state glassy electrolytes.

INTRODUCTION

The possibility of high ionic conduction in glasses was suggested at the beginning of the '70^{1,2}. During the following two decades a large mass of experimental work³, as well as a notable effort of transport modelling⁴ were made. Conductivity values as high as $10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ at room temperature were easily obtained by doping with AgI a number of modified matrices $\text{Ag}_2\text{O}-\text{M}_x\text{O}_y$ ($\text{M}_x\text{O}_y = \text{P}_2\text{O}_5, \text{B}_2\text{O}_3, \text{MoO}_3, \text{Cr}_2\text{O}_7\ldots$)⁵⁻⁸. Likely, the most interesting results from the point of view of basic science were obtained with two of the classical Zachariasen's glass formers, namely B_2O_3 and P_2O_5 , or with their admixture^{9,10}.

Phosphate-based glasses are very interesting from a basic point of view because of some unique properties, like the low glass transition temperature (chiefly in AgI-doped systems) which makes their overall thermal history easily accessible to a large number of experimental techniques. Moreover, the chemistry of phosphorus is well developed after the basic works of Van Wazer¹¹ and Corbridge¹². From the point of view of the applications, phosphate electrolytes may be employed in thin-film sensors and

batteries ¹³, as well as in other electrochemical devices. The research work till 1990 is summarized in an excellent review by Martin ¹⁴, to which this work is largely referred.

In this paper, I will discuss the information on glass structure which is given by ³¹P solid-state NMR. Attention will be chiefly devoted to conducting glasses, but structural and bioactive glasses will be also considered. The NMR bulk information will be related, when necessary, with the results of other experimental and modelling techniques. Although apparently well delimited, the field is rapidly growing on the combined action of new multi-dimensional techniques and sophisticated stochastic approaches like the Reverse Monte Carlo.

THE Q-SITE MODEL APPLIED TO PHOSPHATE GLASSES

An oxide glass in its simplest form is made of at least a former (P_2O_5 in our case), a modifier (generally alkali or silver oxide), and a "dopant" (a salt of the same metal). In general, the addition of the modifier influences the connectivity of the glass former by changing its coordination and/or by creating non-bridging oxygens (NBO). The structure of borate glasses, for example, is quite complex because of the formation of four-fold coordinated borons upon the addition of the modifier ¹⁵.

In contrast, it is quite accepted that under normal pressure conditions phosphorus retains its four-fold oxygen coordination throughout the full composition range from P_2O_5 to the orthophosphate compound M_3PO_4 (M = modifier metal). Obviously, this greatly reduces the number of structural units that can be found in phosphate glasses. A similar structural simplicity holds for silicates, and Lippmaa et. al. ¹⁶ proposed the so-called Q-site model to describe the structural changes induced by the modifier addition. Here, each added monovalent metal forms one NBO around a silicon atom. In principle, at the composition $2M_2O \cdot SiO_2$ all oxygens are non-bridging.

A similar approach was early proposed by Van Wazer for phosphate materials ¹¹. The phosphate groups are shown in Figure 1: Q_3 represents the fully branching unit (three bridging oxygens), Q_2 is the middle unit, Q_1 is the end unit, and Q_0 is the orthophosphate (three NBOs). As the monovalent metal oxide is added to P_2O_5 , the structural units change progressively along the chain $Q_3 \rightarrow Q_2 \rightarrow Q_1 \rightarrow Q_0$, when the ratio

$R = \text{M}_2\text{O}/\text{P}_2\text{O}_5$ goes from 0 to 3. Van Wazer estimated the fractions of the different phosphate units under the assumption that they are controlled by the magnitude of the equilibrium constants, k_i , of the reaction of M_2O with each Q species. The magnitudes of the different k_i determine the amounts of the Q populations.

FIGURE 1. Phosphate groups and related Q names.

While it is quite a simple task to determine the fraction of the individual Q -species in the high-metal range, where the glasses are easy to prepare, it was shown that the only experimental techniques able to work in the low-metal region are X-rays photoelectron spectroscopy (XPS)^{17,18}, ^{31}P MAS-NMR (which will be thoroughly discussed in the next sections) and, at a lower extent, vibrational spectroscopies. Concerning these last techniques, Raman studies appeared to be more numerous, chiefly because the absorption lines are narrower than those of IR spectroscopy. $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$ glasses were studied by Nelson et al.¹⁹, who observed the disappearing of the $\text{P}(=\text{O})\text{O}_3$ symmetric stretch of P_2O_5 at 1390 cm^{-1} when the alkali oxide is added, and the growing of a strong band at $\sim 1150\text{ cm}^{-1}$ attributed to the symmetric stretching of a PO_4^{-1} unit where resonance has equilibrated two non-bridging oxygens, so supporting the idea that the alkali oxide acts in order to depolymerize the phosphate network. Similar results were obtained by Tatsumisago et al.²⁰ on $\text{Li}_2\text{O}:\text{P}_2\text{O}_5$ glasses, and by Scagliotti et al.²¹ on $\text{Li}_2\text{O}:\text{P}_2\text{O}_5$ and $\text{Ag}_2\text{O}:\text{P}_2\text{O}_5$ glasses. However, all these Authors did not prepare glasses in the very low-alkali region. IR spectra of binary phosphate glasses were carefully collected by Risen and co-workers^{22,23}.

Ternary phosphate glasses, chiefly AgI-AgPO₃, were widely studied by the group of Malugani by means of Raman spectroscopy and neutron scattering ²⁴. A review of the many papers written by these Authors is given in ²⁵. The most interesting point they raised is the way AgI enters the phosphate network, where they envisaged the formation of AgI clusters which retain at room temperature the transport properties of α -AgI. This picture, however, is still strongly debated and will be discussed later.

THE EARLY NMR WORKS

Unlike to what happens for borates, the NMR information on phosphate glasses is quite straightforward, chiefly because ³¹P is a 1/2-spin nucleus and the spectra are dominated by chemical shift tensor. Moreover, this nuclide is 100% abundant and very easy to detect. The first MAS-NMR studies were due to Duncan and Douglass ²⁶ and Grimmer and Haubenreisser ²⁷. These works, and others which appeared in the subsequent years ²⁸⁻³¹, allowed to draw a preliminary map of chemical shifts in condensed phosphates, which is shown in Figure 2. In a similar way to what happens in silicates ³², the chemical shift moves towards more positive values when NBOs are added.

FIGURE 2. Chemical shifts in condensed phosphates.

The first systematic works on alkali and silver phosphate and borophosphate glasses are due to the group of Villa³³⁻³⁶. They showed that less polymerized phosphate units are created when the oxide fraction increases. Moreover, they were able to assign the chemical shifts of most mixed B-P units that appear in borophosphates.

More recently, Brow et al. showed that H₂O acts as a modifying oxide in the preparation of phosphate glasses³⁷. They carefully determined water content in Na₂O:P₂O₅ glasses and analyzed their NMR spectra in terms of a pseudobinary system $x(\text{Na}_2\text{O}+\text{H}_2\text{O})(1-x)\text{P}_2\text{O}_5$. As expected, the fraction of end units Q_0 increases with the coordinate x .

AgI:Ag₂O:P₂O₅ glasses were studied by Hayashi and Hayamizu³⁸, who confirmed that the network structure is determined by the last two components, whereas AgI does not modify the network.

Phosphorous-sulphide glasses were thoroughly studied by Eckert et al.^{39, 40}. The Authors showed that addition of P from 5 to 25 mol% causes the formation of a downfield peak at 112 ppm attributed to randomly distributed PS_{3/2} units. The same group performed later a study on Li₂S:P₂S₅ glasses, over the compositional range $0.33 \leq x \text{ Li}_2\text{S} \leq 0.75$. The development of depolymerized units Q_0 , Q_1 and Q_2 was correlated with the Li₂S fraction. For more details on NMR studies of P-S glasses the readers are referred to ref. 14.

THE MOST RECENT DEVELOPMENTS

Alkali phosphate glasses

The structure and the mechanism of lithium conduction in LiCl-Li₂O-P₂O₅-SiO₂ glasses were studied by Tsai et al.⁴¹ by combining ⁷Li, ³¹P and ²⁹Si NMR. The most interesting result of this study is likely that the majority of silicate tetrahedra play a bridging role between different phosphate chains.

Sodium alumino-fluoro-phosphate glasses (Na-P-O-F and Na-Al-P-O-F) were studied by Kirkpatrick and co-workers^{42, 43}. For the aluminum-free series, ¹⁹F MAS-NMR showed the formation of F-P bondings ending the phosphate chains. When aluminium oxide was added, the ¹⁹F spectra showed the formation of F-Al bonding,

while the ^{31}P spectra contained signals of Q_1 sites with one or more Al next-nearest neighbours. The properties of glasses were sensitive to the aluminium coordination, chiefly octahedral for O/P less than 3.5, and tetrahedral for O/P greater than 3.5. The same research group also studied the mixed-alkali effect in Li,Na metaphosphate glasses by combining ^{23}Na and ^{31}P MAS-NMR ⁴⁴. The ^{31}P chemical shifts of Q_2 units became deshielded by increasing the ratio $\text{Na}/(\text{Li}+\text{Na})$, which was rationalized by the Authors in terms of an increased average electron density in the P-O bonds. Both the ^{31}P and ^{23}Na lines displayed greater full widths at half heights for intermediate compositions.

The first NMR study on ultraphosphate glasses is also due to Brow et al. ⁴⁵ who studied the system $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$ for Na_2O contents between 0 and 50 mol%. They found that alkali addition depolymerizes the Q_3 units to form Q_2 sites, in good quantitative agreement with Van Wazer's model. Phosphorus and boron speciation in $(1-y)(\text{K}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2)y(\text{P}_2\text{O}_5)$ was studied by means of ^{11}B and ^{31}P MAS-NMR ⁴⁶. Q_1 and Q_2 units were demonstrated to be the dominant species in the examined composition range ($y \leq 0.03$), while boron coordination was strongly controlled by phosphorus content. Speciation in sodium aluminophosphate glasses was also studied by Abrahams et al. ⁴⁷.

The influence of calcium hydroxyapatite on sodium borophosphate glasses was studied by Ducel et al. ⁴⁸. The increase of calcium was accompanied by the shortening of the phosphate chains. The Authors concluded that the Ca^{2+} ions make crosslinks between the chains.

Zinc-containing sodium phosphate glasses were investigated by the group of Palavit ^{49, 50}. They showed that addition of ZnO to the metaphosphate led to the depolymerization of the chains, with the Zn^{2+} ions preferentially bonded to Q_1 units. More recently, ^1H - ^{31}P CP MAS-NMR was used to study zinc ultraphosphate glasses containing variable amounts of hydroxyl groups ⁵¹. Careful line analyses showed the presence of Q_2 units bonded to H^+ , and of Q_2 units bonded to Zn^{2+} . It was also possible to follow the evolution of the relative fraction sites versus the melting time.

Sodium phosphate glasses containing up to 16 mol% Bi_2O_3 were prepared by a standard quenching technique ⁵². The combined use of IR and ^{31}P MAS-NMR spectroscopies allowed to state that bismuth oxide depolymerizes the glass chains by giving end groups and mixed sodium-bismuth pyrophosphates. The structural role of

Bi_2O_3 in competition with Al_2O_3 was also investigated in $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{Bi}_2\text{O}_3-\text{P}_2\text{O}_5$ glasses⁵³. The glasses were decondensed by both Al^{3+} and Bi^{3+} to give Q_0 and Q_1 units, and the differences in their physico-chemical properties were explained in terms of different anion sizes and polarizabilities. Finally, the structure of gels of the same system was followed by NMR and IR spectroscopies⁵⁴.

Modern two-dimensional solid-state NMR techniques were recently employed by a group in Jena to study short-range order and connectivities in phosphate glasses and glass-ceramics⁵⁵. Among the other results, the Authors showed how chain end units can be distinguished from pyrophosphate groups⁵⁶. A 2D sequence synchronized with MAS rotation allowed to observe a partial chain alignment in extruded metaphosphate glasses⁵⁷. One and two-dimensional heteronuclear ^1H - ^{31}P correlation was used to study the chemistry of water incorporation in sodium phosphate glasses⁵⁸. Up to five different phosphate units were identified in a near-metaphosphate glass after aqueous attack.

$x\text{LiF}-(1-x)\text{LiPO}_3$ pseudobinary glasses were studied for $0 < x < 0.35$ by combining ^1H , ^7Li , ^{19}F and ^{31}P NMR⁵⁹. The addition of LiF leads to a shortening of the chains from 29 to 4 phosphate units. Fluorine gives origin both to end groups and to LiF units, the latter being favoured for high salt contents. ^{31}P spin-lattice relaxation rates for a glass $x = 0.35$ were measured on a wide frequency range by Brinkmann and co-workers⁶⁰.

Silver phosphate glasses

NMR studies on silver phosphate glasses are, to date, still relatively scarce. The structure of the $x\text{Ag}_2\text{SO}_4(1-x)\text{AgPO}_3$ glasses was investigated by means of ^{31}P MAS-NMR Magic Angle Spinning (MAS) and other techniques⁶¹. For $x < 0.2$ the sulphate modifies the phosphate, and preferentially occupies a bridging position between two Q_1 units. In the sulphate-rich glasses, in contrast, a substantial fraction of Ag_2SO_4 goes into interstitial positions. This structural description qualitatively agrees with conductivity, acoustic attenuation, and thermal data. In particular, acoustic attenuation results suggested that silver is very mobile near the interstitial sulphates, but that its long range diffusion is controlled by slower processes.

The mechanisms of ion diffusion and the structural role of Ag_2S in $\text{Ag}_2\text{S}:\text{AgPO}_3$ glasses were also studied ⁶². By comparing conductivity and ultrasonic attenuation data, a number of microscopic parameters for Ag^+ diffusion were derived. These glasses have a behaviour intermediate between that of AgI -doped and network-modified glasses. The implication that the sulphide acts both as an interstitial dopant and as a network modifier was confirmed by ^{31}P MAS-NMR, which revealed a complex scheme of reaction between the sulphide and the metaphosphate.

Silver metaphosphate glass, AgPO_3 , prepared by quenching a melt of AgNO_3 and $\text{NH}_4\text{H}_2\text{PO}_4$, was carefully studied by means of thermal analysis and ^{31}P MAS-NMR ⁶³. It was shown that the amount of structural water, which acts as a modifying oxide, is strongly related to the temperature of the melt, and to the time it spends at that temperature. In contrast, samples obtained by melting AgPO_3 crystals prepared as described in ref. 64 showed a nearly meta- composition.

The multiplicity of the NMR spectra of glassy and crystalline AgPO_3 was recently discussed ⁶⁵, in order to clarify some controversial results reported in a work on phosphomolybdate glasses ⁶⁶. It was shown that the Q_2 doublet appearing in the spectrum of AgPO_3 crystal is due to crystallographically non-equivalent P atoms.

Beside some partial results in ref. 66, to our knowledge the only NMR study on $\text{AgI}:\text{Ag}_2\text{O}:\text{P}_2\text{O}_5$ has been reported by the group of Jena ⁶⁷. By using double-quantum and radio-frequency dipole recoupling NMR, they showed that the effect of AgI on the phosphate structure is chiefly to increase the distances between the phosphorus chains, in agreement with the modified random network model ⁶⁸, and with the neutron diffraction data combined with Reverse Monte Carlo simulations of Swenson et al. ⁶⁹. These conclusions go to enrich the interesting and long-life debate on the structural role played by AgI in fast ionic conducting (FIC) glasses $\text{AgI}:\text{Ag}_2\text{O}:\text{M}_x\text{O}_y$ ($\text{M}=\text{P}, \text{B}, \text{Mo}, \text{Cr}, \text{W}$). While, in fact, it is quite accepted that Ag^+ experiences a mixed I/O coordination sphere in molybdates ⁷⁰, different points of view were also recently presented for borates and phosphates. For example, Kamitsos et al. interpreted their IR data as describing a tendency of AgI to form microdomains which increases with the AgI content ⁷¹. In contrast, a cluster model was found not necessary to explain ionic conduction in

AgI:AgPO₃ glasses ⁷², and also considered unlike on the basis of pure thermodynamic considerations, at least for lower P₂O₅/Ag₂O ratios ⁷³.

Other phosphate glasses

Binary alkaline-earth glasses of ultraphosphate composition were studied by Losso et al ⁷⁴. The behaviour of the chemical shift tensors of Q_2 and Q_3 units was discussed in terms of the changes of bridging and dihedral angles between the phosphate tetrahedra, as well as by changes of the position of the cations. The same group also studied calcium-sodium phosphates glasses and glass-ceramics modified with MgO and Al₂O₃ ⁷⁵. The structure of the samples was analyzed as a function of the modifying oxides, and the Q_2 content during heat treatment was discussed. More recently, calcium phosphate glasses were studied by means of double-quantum ³¹P NMR ⁷⁶. The Authors showed that it is possible to analyze the chain length distribution, as well as to separate chemically different Q_1 or Q_2 units (e.g. middle groups of long chains or rings) on the basis of their isotropic chemical shift.

Bioactive calcium phosphate glasses and glass-ceramics, obtained in the pyrophosphate region with addition of Na₂O and TiO₂, were studied by ³¹P NMR and Raman spectroscopy ⁷⁷. The crystallization processes in MgO-CaO-SiO₂-P₂O₅ bioactive glasses were investigated by means of ²⁹Si and ³¹P MAS-NMR ⁷⁸. It was shown that ZnO can make the glass stable against crystallization at low temperature.

Lead-zinc phosphate glasses in the region 30-50 mol% P₂O₅ were investigated by means of Raman and ³¹P MAS-NMR spectroscopies ⁷⁹. It was shown that both ZnO and PbO play a dual structural role (network former and modifier) depending on the glass composition. The role of modifier is favoured for high P₂O₅ contents. A lead-barium alumino-phosphate glass was also studied by ²⁷Al and ³¹P MAS-NMR ⁸⁰. Finally, alumino-phosphate sealing glasses were recently studied ⁸¹.

SUMMARY

In this paper I reviewed most of the recent NMR studies on phosphate glasses, chiefly in order to show the potential of the technique to give information on disordered systems. For this reason a fully critical approach was avoided.

It seems that ^{31}P MAS-NMR has become a quasi-routine tool to investigate the short-range structure of phosphate glasses and glass-ceramics. Nevertheless, the most recent developments of 2D multiple quantum experiments, as well as of other sophisticated sequences for interaction decoupling-recoupling, will offer to the scientist a renewed arsenal to open windows on medium-range order, and to investigate the relationships among structural stability, phase separation, nucleation, wetting, interfacial energy and conduction.

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