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Alkali and alkali–lead oxynitride phosphate glasses: a comparative structural study by NMR and XPS

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Abstract – Nitrided phosphate glasses are characterized by tetrahedral units $P(O,N)_4$ in which nitrogen atoms have substituted for both bridging and non-bridging double bonded oxygen atoms. ^{31}P magic angle spinning (MAS) nuclear magnetic resonance (NMR) shows that PO_4, PO_3N and PO_2N_2 tetrahedra may coexist within the glass network. The relative proportion of these structural units as a function of the N/P ratio depends on the composition of the oxide base glass, as illustrated in sodium, lithium–sodium and lithium–sodium–lead phosphate glasses. Furthermore, ^{31}P double quantum (DQ) MAS NMR shows that the nitrogen/oxygen substitution is not a random process. The modifier cations influence the connections between tetrahedra throughout the overall nitrided glass network, and, therefore, the final structure. N_{1s} X-ray photoelectron spectroscopy (XPS) shows that nitrogen atoms may exist in the $P(O,N)_4$ tetrahedra as doubly coordinated (–N=) and triply coordinated (–N<) species, bonded to two and three phosphorus atoms, respectively. The relation between both kinds of nitrogen as a function of the N/P ratio depends also on the oxide-base glass composition. In this work, the thermal nitridation in flowing ammonia of alkali and alkali–lead metaphosphate glasses is studied. The results deduced from the NMR and XPS experiments make it possible, in addition to a comparison between the nitridation kinetics, to follow and to compare the structural evolution of oxynitride glasses resulting from a progressive nitrogen incorporation. In particular, the important role of PbO in the nitridation mechanism is revealed, demonstrating in this case that the nitridation is not random, its beginning included. ***To cite this article: F. Muñoz et al., C. R. Chimie 5 (2002) 731–738*** © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

oxynitride glasses / nitridation / phosphates / alkali / lead / ^{31}P NMR / N_{1s} XPS

Résumé – Les verres azotés de phosphates sont caractérisés par des entités tétraédriques $P(O,N)_4$, dans lesquelles les atomes d'azote ont substitué à la fois des atomes d'oxygène pontants et non pontants, doublement liés. L'étude RMN MAS du phosphore ^{31}P montre que des tétraèdres PO_4, PO_3N et PO_2N_2 coexistent dans le réseau vitreux. Leur proportion relative est fonction du rapport N/P et dépend de la composition chimique du verre oxyde de base, comme il est montré dans le cas de verres de phosphates à base de sodium, lithium–sodium et lithium–sodium–plomb. Par ailleurs, l'étude RMN MAS double quanta du phosphore ^{31}P montre que la substitution de l'oxygène par de l'azote ne s'effectue pas de façon aléatoire. Les cations modificateurs influencent notablement la connectivité entre les différentes unités structurales, et par là-même la structure du réseau vitreux azoté. La spectroscopie XPS N_{1s} montre que les atomes d'azote des tétraèdres $P(O,N)_4$ peuvent être doublement (–N=) ou triplement (–N<) coordinés, c'est-à-dire liés à deux ou trois atomes de phosphore. Leur proportion respective est fonction non seulement du rapport atomique N/P, mais, là aussi, de la composition du verre oxyde de base. Dans ce travail est étudiée la nitruration par l'ammoniac de verres de métaphosphates alcalins et alcalins–plomb. Les résultats des études RMN et XPS permettent, en plus de la comparaison des cinétiques de nitruration, de suivre et de comparer l'évolution structurale de verres oxynitrures issus de l'incorporation progressive d'azote. En particulier, le rôle du plomb dans le mécanisme de nitruration est mis en évidence, démontrant ainsi que la nitruration n'est pas aléatoire, y compris, dans ce cas, au début de la substitution azote/oxygène. ***Pour citer cet article : F. Muñoz et al., C. R. Chimie 5 (2002) 731–738*** © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

verres azotés / nitruration / phosphates / alcalins / plomb / RMN ^{31}P / XPS N_{1s}

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1. Introduction

Phosphate glasses are of great technological interest due to specific thermal properties, i.e. low glass transition and dilatometric softening temperatures, and high thermal expansion coefficients, which make them ideal as low-temperature sealing glasses [1–5]. The problem is their low chemical durability, often associated [6]. However, the nitridation ability of these glasses under ammonia atmosphere, demonstrated as soon as 1982 [7], is a suitable way to improve their chemical resistance.

The structure of metaphosphate glasses consists of $–PO_4–PO_4–$ chains of tetrahedra, interconnected through modifier cations. The middle tetrahedra, named Q^2-groups according to Lippma et al.'s notation [8], have two bridging oxygens (BO), bonded to neighbouring phosphorus atoms, and two non-bridging oxygens (NBO).

During nitridation in ammonia, P–N bonds form at the expense of P–O bonds, nitrogen substituting within PO_4 tetrahedra for both bridging and non-bridging double-bonded oxygens to form PO_3N and PO_2N_2 tetrahedra, as proved by ^{31}P Nuclear Magnetic Resonance (NMR) [9, 10]. Moreover, X-ray Photoelectron Spectroscopy (XPS) results have shown that nitrogen atoms exist as two-coordinated, $–N=(N_d)$, and three-coordinated, $–N<(N_t)$ species [10–12]. As a result of the nitrogen/oxygen substitution, the cross-linking density and the covalency of the glass network increase, which improves effectively the glass durability.

Two different models have been proposed to explain the nitridation mechanism. Reidmeyer et al. [13] have assumed that the N/O substitution is a random process. On the opposite, Le Sauze et al. [9] have described the nitridation of the $Li_{0.5}Na_{0.5}PO_3$ glass by oxynitride microdomains growing progressively at the expense of oxide ones, where PO_2N_2 tetrahedra appear by substituting preferentially bridging oxygens shared by a PO_4 tetrahedron and a PO_3N tetrahedron. In both cases, it is concluded that non-bridging oxygens coordinating modifier cations are not substituted.

The higher field strength of divalent compared to monovalent modifier cations results generally in higher values of melt viscosity, which leads to a limited nitridation, for example when BaO is introduced in the starting glass formulation. PbO is an exception as its introduction provides a low melt viscosity and thus enables incorporation of high nitrogen contents, as shown by Pascual et al. [14, 15]. Moreover, the presence of Pb^{2+} cations improves the glass chemical durability while maintaining low softening points [16], thus making lead-containing glasses appropriate materials for soldering applications.

This paper deals with the thermal nitridation in flowing ammonia of alkali and alkali–lead metaphosphate glasses. In addition to a comparison between the nitridation kinetics, ^{31}P Magic Angle Spinning (MAS) NMR and Double Quantum (DQ)-MAS NMR, and XPS results have been used to compare the structural evolution resulting from progressive nitrogen incorporation.

2. Experimental

The oxide-base glass compositions 50 Na_2O·50 P_2O_5 ('NaPO'), 25 Li_2O·25 Na_2O·50 P_2O_5 (LiNaPO) and 12.5 Li_2O·12.5 Na_2O·25 PbO·50 P_2O_5 ('LiNaPbPO'), in mol%, were prepared by melting, according to a previously described procedure [17, 18]. Phosphorus oxynitride glass samples, 'NaPON', 'LiNaPON' and 'LiNaPbPON', were prepared by thermal treatment of the base glasses in flowing anhydrous ammonia, at temperatures ranging from 600 to 750 °C for times up to 96 h, as previously described [17, 18].

Nitrogen analyses were carried out in a nitrogen/oxygen LECO TC-436 analyser by the inert gas fusion method, with a maximum deviation in the N/P atomic ratio of ±0.02. The nitrogen content was confirmed by direct chemical analysis as NH_3, according to the Grekov method [19].

^{31}P MAS NMR spectra were recorded on a Bruker ASX 100 spectrometer operating at 40.48 MHz (2.34 T). The pulse length was 3.0 μs (π/2) and 120 s delay time was used. The spinning rate was 15 kHz. The ^{31}P spectra were fitted to Gaussian functions, in accordance with the chemical shift distribution of the amorphous state. The precision of the relative component determination was ±0.5%.

^{31}P Double Quantum MAS NMR measurements were performed at 2.34 T, using a previously described procedure [20, 21]. A 4 mm MAS probe was used at a MAS frequency of 12.5 kHz. The BaBa (back to back) sequence was applied, using TPPI (time proportional phase increment) [20–22]. A 3-μs pulse was used (π/2), and a 5 s recycling delay. Sixty-four t_1 increments of 80 μs were used, with 32 accumulations per slice.

XPS measurements were performed on a CAMECA RIBER SIA 200 electron spectrometer for multi-technique surface analysis system. This system is equipped with a MAC 2 CAMECA RIBER double stage cylindrical mirror electron-energy analyser. The photon source was a CAMECA SCX 700 dual anode X-ray source. A non-monochromatized Al Kα X-ray source ($h\nu$ = 1486.6 eV) was used as the excitation source in all cases. A spectrometer energy calibration was made by using the Au $4f^{7/2}$ and Cu $2p^{3/2}$ photo-

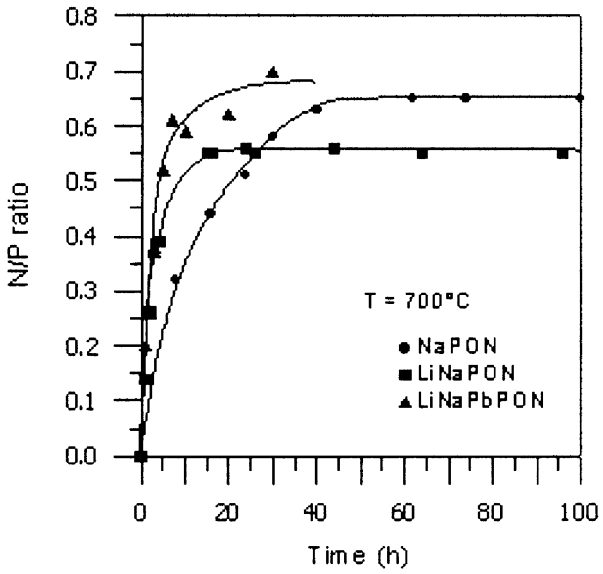

Fig. 1. Nitridation kinetics at 700 °C of NaPON, LiNaPON and LiNaPbPON glasses. The lines are only a guide for the eyes.

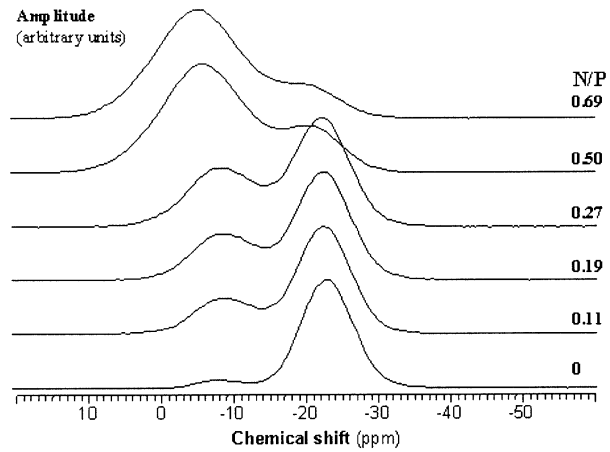

Fig. 2. ^{31}P MAS NMR spectra of $Li_{0.25}Na_{0.25}Pb_{0.25}PO_{3-3x/2}N_x$ glasses ($0 \le x \le 0.69$).

electron lines. Due to surface electrostatic charges detected for some samples and resulting in variable retarding effects, all the energy scales corresponding to the XPS spectra reported in this paper were normalized from the energy position of the C_{1s} photoelectron line of atmospheric carbon $(CH_2)_n$: 285 eV. The photoemission measurements were carried out on a series of samples before and after removing the surface carbon contamination by ion sputtering. The sputtering was performed for 10 min in the UHV (ultra high vacuum) analysis chamber with a 0.6 keV Ar^+ ion beam (30 mA cm^{-2}). The elemental composition of the samples was evaluated using the integrated areas of the core-level peaks O_{1s}, C_{1s}, P_{2p}, Pb_{4f}, Na_{1s} and N_{1s}. The Li atomic concentration could not be measured due to the very low value of the ionisation cross-section for this element.

3. Results

3.1. Nitridation kinetics

Fig. 1 shows the progressive nitrogen enrichment of NaPON, LiNaPON and LiNaPbPON glasses as a function of nitridation time at $T = 700$ °C. For the three different base glasses studied, the nitrogen content reaches an asymptotic limit, which is different for each composition. The time after which this limit is reached, i.e. the nitridation rate, depends also on the starting glass composition.

3.2. ^{31}P MAS NMR

The ^{31}P MAS NMR spectra of the $NaPO_3$, $Li_{0.5}Na_{0.5}PO_3$ and $Li_{0.25}Na_{0.25}Pb_{0.25}PO_3$ base glasses contain a single peak at –20.7, –21.4 and –23 ppm, respectively. According to Sato et al. [23], this resonance corresponds to Q^2-type sites. From the previously reported chemical shifts, Q^2(Na): –19 ppm [23], Q^2(Li): –23 ppm [9] and Q^2(Pb): –24.5 ppm [24], and considering an average distribution of the cations around the Q^2 sites, we calculate Q^2 (Li, Na) and Q^2 (Li, Na, Pb) values of –21 ppm and –22.8 ppm for the $Li_{0.5}Na_{0.5}PO_3$ and $Li_{0.25}Na_{0.25}Pb_{0.25}PO_3$ glass compositions, respectively, in agreement with the experimental results.

As N/P increases, two new resonances can be observed in the ^{31}P MAS NMR spectra of the nitrided glasses in addition to the Q^2-type resonance mentioned above, which are assigned to PO_3N (~–10 ppm) and PO_2N_2 (~0 ppm) tetrahedra [9, 10, 24]. As an example, Fig. 2 shows the ^{31}P NMR spectra of LiNaPbPON glasses.

For the three studied series, PO_3N and PO_2N_2 tetrahedra appear at the expense of PO_4 tetrahedra. Fig. 3 shows the variation of the relative proportions of the three kinds of tetrahedra as a function of the N/P ratio.

The PO_4 percentage (Fig. 3a) does not decrease at the same rate as the N/P ratio increases. For N/P < ~0.2, the proportion of remaining PO_4 tetrahedra is similar for the three glass series. At higher N/P, it follows the sequence NaPON > LiNaPbPON > LiNaPON.

As shown in Fig. 3b, PO_3N tetrahedra appear as soon as nitrogen is incorporated within the glass network, and, in all cases, their proportion versus N/P increases asymptotically up to a maximum value, which depends on the starting glass composition. In the alkali phosphate glasses, the percentages of PO_3N are similar for N/P < ~0.3, then diverge at higher nitrogen contents to reach a maximum around 36%

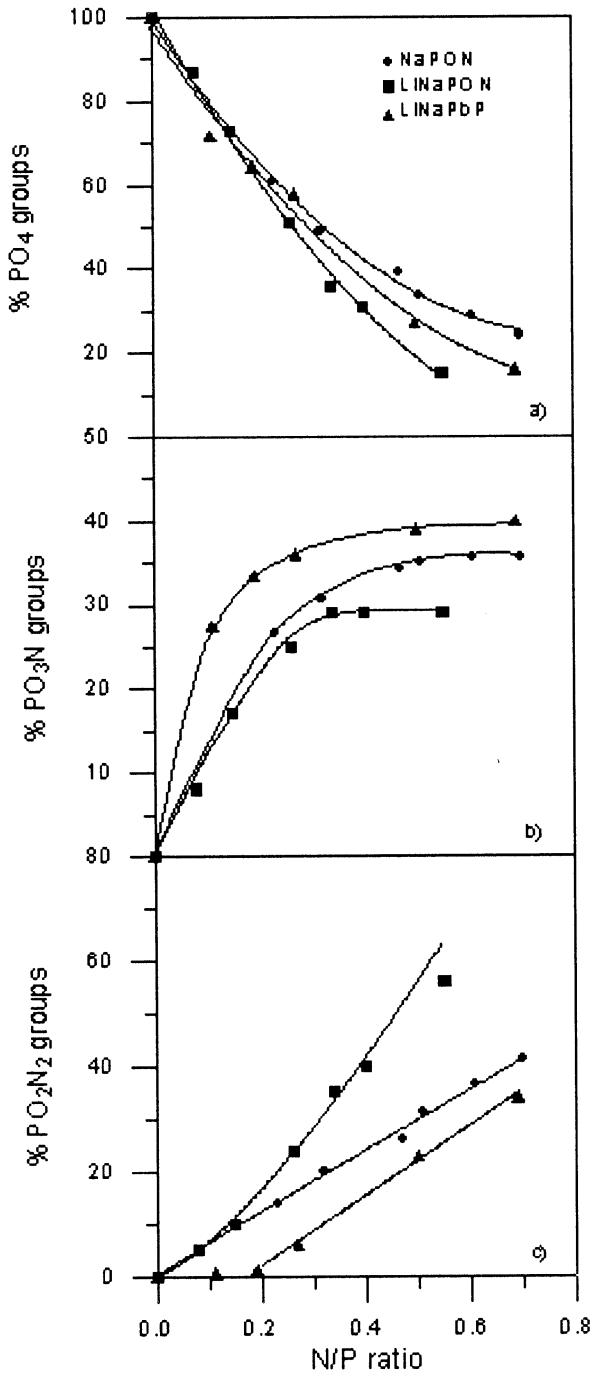

Fig. 3. Variation of the percentages of $P(O,N)_4$ units as a function of the N/P ratio in NaPON, LiNaPON and LiNaPbPON glasses: (**a**) PO_4, (**b**) PO_3N and (**c**) PO_2N_2 tetrahedra. The lines are only a guide for the eyes.

and 29% in NaPON and LiNaPON glasses, respectively. In LiNaPbPON glasses, much higher percentages of PO_3N are observed from the beginning of nitridation, with a final value of ~40%.

The three glass series show also a different evolution of their PO_2N_2 tetrahedra when the nitrogen content increases (Fig. 3c). In NaPON and LiNaPON glasses, the percentages of PO_2N_2 only coincide at low nitrogen contents (N/P ~ 0.15), their increase following a straight line for NaPON with a maximum around 41% for N/P ~ 0.7, whereas much higher percentages, around 56% for N/P = 0.55, are reached in LiNaPON glasses.

On the other hand, in LiNaPbPON glasses the PO_2N_2 proportion remains close to zero for N/P < ~0.2, then increases rapidly up to a maximum of ~34% for N/P = 0.69. Whatever the considered system, the slope of the corresponding variation curve is never decreasing, even at high nitrogen contents.

3.3. ^{31}P DQ-MAS NMR

The ^{31}P DQ MAS-NMR spectrum of the $Li_{0.5}Na_{0.5}PO_{2.17}N_{0.55}$ nitrided glass sample, which is the LiNaPON nitrogen-richest composition, is presented in Fig. 4a. In addition to an auto-correlation peak A–A, at approximately –40 ppm, which is characteristic of a dipolar connectivity between PO_4 tetrahedra, it indicates connectivity between PO_3N and PO_2N_2 tetrahedra (auto- and cross-correlations at –5, –15 and –22 ppm). It reveals also A–B and A–C cross-correlations, i.e. the existence of direct links between pure oxygenated PO_4 tetrahedra and partially nitrided ones.

The ^{31}P double quantum spectrum of the $Li_{0.25}Na_{0.25}Pb_{0.25}PO_{2.25}N_{0.5}$ glass (Fig. 4b) shows several differences compared to the LiNaPON glass. It shows a contribution on the diagonal at –21 ppm in the MAS dimension, which can be assigned to PO_4–PO_4 auto-correlation. The two off-diagonal resonances at –22 and –8 ppm can be attributed to cross-correlation peaks due to connectivity between PO_4 and PO_3N tetrahedra. Two other off-diagonal resonances are also detected at –8 and –5 ppm and attributed to PO_3N–PO_2N_2 cross-correlations. At high nitrogen content, N/P = 0.69, the ^{31}P DQ-MAS NMR spectrum (Fig. 5) shows that some PO_4–PO_4 connections still remain along with off-diagonal peaks at –7.5 and –3 ppm, corresponding to PO_3N–PO_2N_2 connections. No auto-correlations PO_3N–PO_3N or PO_2N_2–PO_2N_2 are observed in the LiNaPbPON glasses, even at the highest N/P ratios. In addition, a weak resonance is also detected on the isotropic projection, with a chemical shift of +4 ppm in the MAS dimension, which is attributed to the presence of Q^1 sites of pyrophosphate-type [25].

3.4. N_{1s} XPS

Fig. 6a,b shows the N_{1s} XPS spectra of two representative oxynitride glass compositions, $Li_{0.25}Na_{0.25}Pb_{0.25}PO_{1.97}N_{0.69}$ (Fig. 6a) and

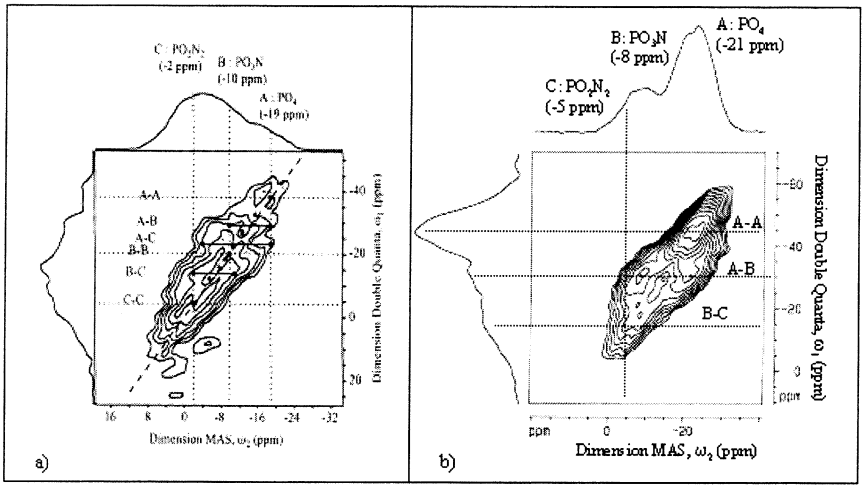

Fig. 4. ^{31}P DQ–MAS NMR spectra of (**a**) $Li_{0.5}Na_{0.5}PO_{2.17}N_{0.55}$ and (**b**) $Li_{0.25}Na_{0.25}Pb_{0.25}PO_{2.25}N_{0.50}$ glasses.

$Li_{0.5}Na_{0.5}PO_{2.17}N_{0.55}$ (Fig. 6b), which can be decomposed into two Gaussians located at ~ 397.7 and ~ 399.4 eV. They have been previously assigned to the two different bonding states of nitrogen, i.e., respectively, –N=(N_d) nitrogen atoms, bonded to two phosphorus atoms, and –N<(N_t) nitrogen atoms, bonded to three phosphorus atoms [11, 12, 26, 27].

The variation of the N_d/P and N_t/P atomic ratios versus increasing N/P (as obtained by XPS) is shown in Fig. 7a and 7b for the three glass series. Both types of nitrogen are always present from the beginning of nitridation, and in all cases the variation of N_d/P or N_t/P follows the same trend: the N_t atoms are first predominant before to become in a minority, because the slope of their variation curve decreases progressively with increasing N/P, whereas that of N_d regularly increases.

As can be seen in Fig. 8, the variation of the N_t/N_d ratio depends on the nature of the glass. Whereas a practically linear decrease is observed for the NaPON

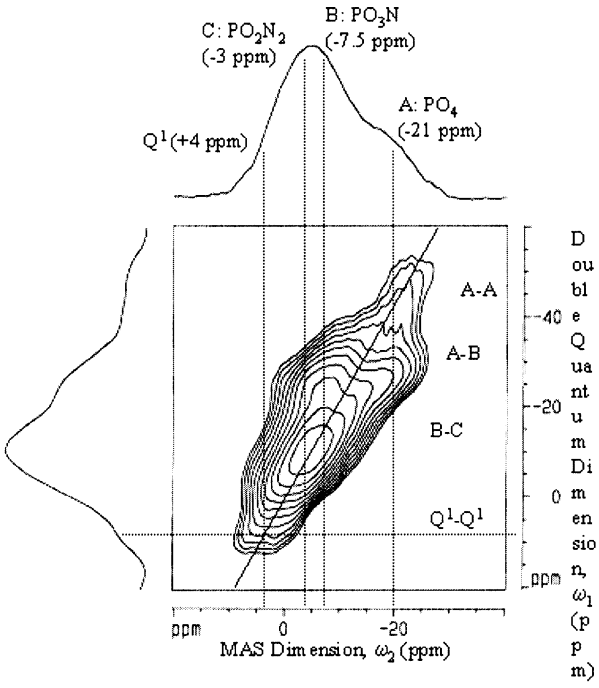

Fig. 5. ^{31}P DQ–MAS NMR spectrum of the $Li_{0.25}Na_{0.25}Pb_{0.25}PO_{1.97}N_{0.69}$ glass.

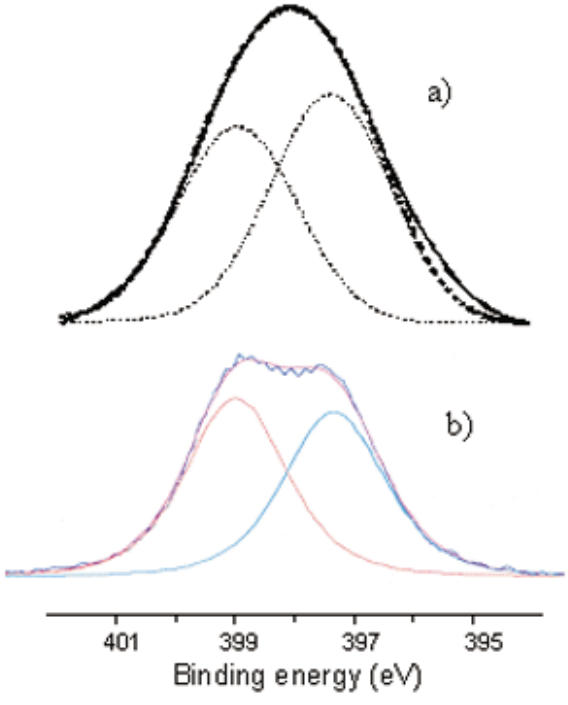

Fig. 6. N_{1s} XPS spectra of (**a**) $Li_{0.25}Na_{0.25}Pb_{0.25}PO_{1.97}N_{0.69}$ and (**b**) $Li_{0.5}Na_{0.5}PO_{2.17}N_{0.55}$ glass compositions.

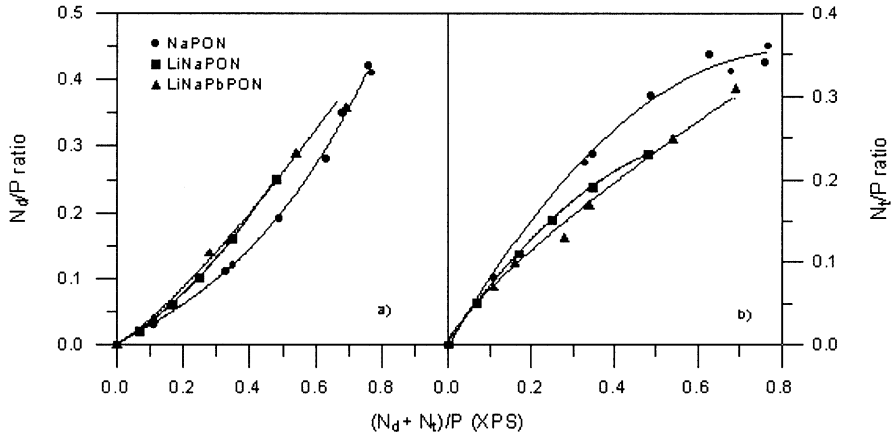

Fig. 7. (**a**) N_d/P ratios and (**b**) N_t/P ratios, versus total nitrogen content, taken from XPS data, for the three NaPON, LiNaPON and LiNaPbPON glass systems. The lines are only a guide for the eyes.

glasses, the mixed-alkali glasses, LiNaPON and LiNaPbPON give a similar variation, with in both cases a fast decrease during the first nitridation stage.

4. Discussion

Fig. 1, which represents the nitridation kinetics, clearly shows a dependence on the base glass composition. On the one hand, the time after which the maximum nitrogen content is reached is shorter for LiNaPON and LiNaPbPON glasses, which have lower glass transition temperatures, and therefore lower melt viscosities, than NaPON glasses [18, 23], which is in accordance with a diffusion-controlled nitridation mechanism. On the other hand, the value of the maximum is clearly a function of the glass composition. In particular, although the nitridation rate is higher in the less viscous LiNaPON glasses than in NaPON glasses, their maximum nitrogen content is lower.

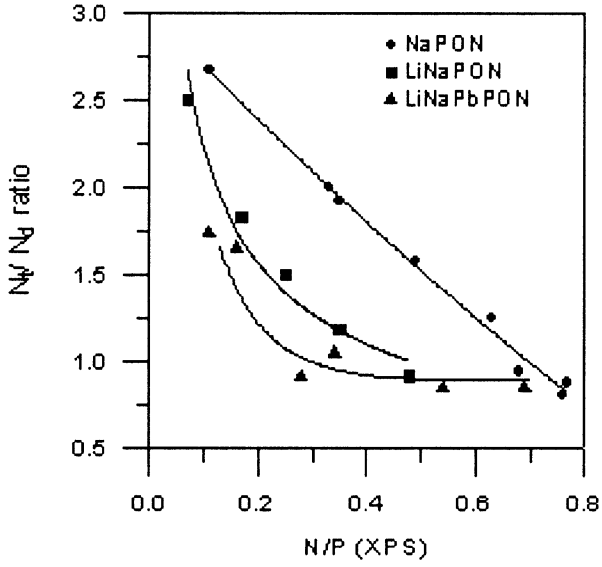

Fig. 8. N_t/N_d ratio versus total nitrogen content, taken from XPS data, for the three NaPON, LiNaPON and LiNaPbPON glass systems. The lines are only a guide for the eyes.

For the three systems, the proportion of PO_3N tetrahedra as a function of the nitrogen content (Fig. 3b) reaches an asymptotic maximum value and, since that of PO_4 tetrahedra decreases regularly along the whole oxynitride domain (Fig. 3a), it looks like that, from a certain N/P value, PO_2N_2 tetrahedra form directly at the expense of PO_4. The interconnections between the different $P(O,N)_4$ tetrahedra, observed by DQ-MAS NMR, imply existence of both pure oxide and oxynitride microdomains within the glass network. So, the limit in the PO_3N percentage can be explained by a nitrogen/oxygen substitution affecting preferentially bridging oxygen atoms shared by a PO_4 tetrahedron and a PO_3N tetrahedron at the boundaries between microdomains. It results in a simultaneous formation of both a PO_3N and a PO_2N_2 units. In other words, formation of one PO_2N_2 tetrahedron at the expense of a PO_3N is accompanied by formation of another one PO_3N at the expense of a PO_4, and, consequently, the number of PO_3N tetrahedra remains constant. According to this scheme, the N/O substitution would not be a random process during the intermediate and final nitridation stages. However, a purely random substitution cannot be excluded during the first stage.

This nitridation process turns different in LiNaPbPON glasses, which is attributable, of course, to lead atoms. The fast increase in the proportion of PO_3N tetrahedra with increasing N/P, together with an absence of PO_2N_2 before the maximum PO_3N percentage is reached, indicates their preferential formation at the beginning. In addition, there are neither PO_3N–PO_3N nor PO_2N_2–PO_2N_2 connections in the corresponding DQ–MAS NMR spectra. The scheme that we propose in this case [24] assumes that, at first, PO_4 tetrahedra located in the vicinity of lead atoms are preferentially nitrided and rapidly transformed into

PO_3N. Only once all of these PO_4 are converted into PO_3N units, the other PO_4 tetrahedra as well as the PO_3N are substituted to form PO_3N and PO_2N_2 units, respectively. The high PbO concentration of the base glass along with the high coordination number of Pb^{2+} ions would explain the fast increase in PO_3N tetrahedra, as well as their higher percentage at the highest N/P ratios than in the NaPON and LiNaPON glasses.

XPS results show that the N_t species are systematically predominant at the beginning of nitridation. However, the N_t/N_d ratio decreases as a function of nitrogen content, showing a different behaviour depending on glass composition (Fig. 8). The decrease is faster for LiNaPbPON glasses. As it has been already proved [17], the N_t/N_d ratio does not depend on the melt viscosity, but it should be better correlated with structural aspects induced by the nature of modifier cations. At the beginning of nitridation, the formation of N_t nitrogen atoms, assumed to only affect bridging oxygen atoms (BO), proceeds more rapidly, probably because it is easy to replace BO atoms after the cut of P–O–P bonds within the metaphosphate chains. On the opposite, formation of N_d nitrogen atoms requires both bridging and non-bridging (NBO) oxygen atoms [12]. The progressive decrease observed in the formation rate of N_t atoms is explainable by steric effects resulting from the higher cross-linking they induce compared to N_d atoms. The faster decrease of N_t/N_d in LiNaPON and LiNaPbPON than in NaPON glasses could indicate that the greater structural complexity of a multi-cation glass network, associated to the high coordination number of large modifier cations such as Pb^{2+}, is favourable to the formation of N_d species. Further work is now in progress to clarify the structural role of lead by introducing different PbO contents in the Li–Na–Pb–P–O–N system.

On the other hand, the presence in the lead-containing glasses of PO_3N tetrahedra as the only nitrided structural units up to $N/P \sim 0.2$ confirms that these PO_3N tetrahedra form from the two kinds of nitrogen, N_d and N_t, since both species coexist from the very beginning of nitridation. An ideal situation for a complete understanding of the nitridation mechanism would be, of course, to closely correlate the NMR and the XPS data, for example to be able to differentiate a PO_3N tetrahedron containing a N_d atom from a PO_3N containing a N_t atom, and to distinguish also between the three different possible PO_2N_2 tetrahedra.

5. Conclusion

In this study, a comparison was made between three different series of oxynitride phosphate glasses, NaPON, LiNaPON and LiNaPbPON, concerning their ability to nitridation and their structure, investigated by NMR and XPS. The results show that, if all the glasses are composed of PO_4, PO_3N and PO_2N_2 coexisting tetrahedral units, with both two- and three-coordinated nitrogen atoms, they can present significant differences which originate either from different melt viscosities or from structural aspects related to the nature of the modifier cations.

The nitridation mechanism proposed for LiNaPON glasses, assumed as an initial random N/O substitution followed by a progressive growing of nitrided microdomains from oxide ones, changes with introduction of lead. In this case, it is thought that the nitridation is not random since its beginning. The Pb^{2+} ions induce nitrogen/oxygen substitution in all the PO_4 tetrahedra surrounding lead atoms, thus giving rise only to PO_3N tetrahedra before any formation of PO_2N_2.

The other relevant difference between these systems is the faster decrease of the N_d/N_t ratio in LiNaPON and LiNaPbPON than in NaPON glasses. This could indicate that the greater is the structural complexity of the glass network and the steric hindrance introduced by large modifier cations such as Pb^{2+}, the easier is the formation of N_d nitrogen atoms.

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