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Study of aluminophosphate oxynitride (AlPON) materials by X-ray photoelectron (XPS) and diffuse reflectance Fourier transform IR spectroscopy (DRIFTS)

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A series of amorphous aluminophosphate oxynitrides (AlPON) have been obtained by nitridation of $AlPO_4$ in a tubular furnace at 750 °C under a dry NH_3 stream. Bulk nitrogen content is controlled by the reaction time and quantified by alkaline digestion with molten KOH. Samples have been analysed by X-ray photoelectron spectroscopy (XPS) and diffuse reflectance IR spectroscopy (DRIFTS). XPS results indicate that nitrogen selectively replaces oxygen atoms bonded to phosphorus in the $[PO_4]$ tetrahedra of $AlPO_4$ leading to a mixture of $[PO_xN_{4-x}]$ units in AlPON. Simultaneously, an Al_2O_3-type phase develops. Compositions obtained by XPS are in good agreement with those expected from bulk formulation. Nitridation reaction starts at the surface of $AlPO_4$ by breaking P—O bonds and generating terminal $P—NH_2$. Once surface $P—NH_2$ saturation is achieved (above 3.6 mass% N), bulk nitridation occurs. In nitrogen saturated AlPON samples (*ca.* 20 mass% N) the presence of a surface P_3N_5 phase is proposed to be responsible for the slight surface nitrogen enrichment observed. The presence of structural (—NH—) groups, isoelectronic to (—O—), and their growing concentration with nitridation time have been detected by DRIFTS. Diffuse reflectance IR spectroscopy also suggests the presence of cyclic (P—N—P) structures.

Nitridation has been used as a method to improve specific physical properties of phosphates.[1,2] However, nitrogen incorporation to the $AlPO_4$ framework is also a route to modify important chemical properties such as the resistance to hydrolysis or the surface basicity.[3–5] The combination of the enhanced surface basicity and the high specific area of aluminophosphate oxynitrides (AlPON) has led to their use as catalysts and catalysts supports in base-catalysed processes.[6,7]

Aluminophosphate oxynitrides (AlPON) are amorphous materials obtained by nitridation of amorphous $AlPO_4$. From the structural point of view, and based on the maintenance of texture upon nitridation, it is presumed that oxygen replacement by nitrogen does not modify the short range structure of the amorphous $AlPO_4$ precursor. AlPON materials are then built up of alternating $[PO_4]$ and $[AlO_4]$ tetrahedra in which nitrogen partially replaces oxygen ($AlPO_{4-3/2x}N_x$). There is also some contribution of $[AlO_5]$ and octahedral $[AlO_6]$.[8–10]

The amorphous character of AlPON makes their complete structural characterisation difficult. However, a combination of X-ray photoelectron spectroscopy (XPS) and diffuse reflectance Fourier transform IR spectroscopy (DRIFTS) has provided some results that have been supported by XANES (X-ray absorption near edge spectroscopy).[5]

More recently, the short range structure of AlPO systems (formally $AlPO_4$–Al_2O_3) with variable P/Al ratio has been modelled, by similarity with cyclic metaphosphates, with six-membered cyclic clusters with alternating P—O—(P,Al) bonds.[11] The applicability of this model to amorphous phosphate oxynitrides (AlPON) is supported by the existence of a crystalline phase $Na_3AlP_3O_9N$ in which six-membered rings with alternating P—N—P and P—O—(P,Al) bonds are identified.[12] *Ab initio* calculations on cyclic clusters have succeeded in predicting XPS and DRIFTS spectra of AlPO systems[11] and is revealed as a powerful tool to be considered in the determination of the short range structure of AlPON materials.

In this article we focus on the characterisation of a series of amorphous AlPON solids with a nitrogen content ranging from 2.8 up to 20% (by mass) using XPS and diffuse reflectance IR spectroscopy (DRIFTS). Results obtained here will be a reference for future modelling.

Experimental

Sample preparation

Aluminophosphate oxynitrides (AlPONs) are obtained by nitridation of $AlPO_4$ precursor in a dry NH_3 stream at 750 °C in a tubular furnace. The reaction extent is strongly influenced by many factors such as the precursor mass, NH_3 flow, temperature, time of contact and the capability of AlPON undergoing hydrolysis. A relatively high NH_3 flow ($30\ l\ h^{-1}$) through a narrow tubular furnace (i.d. = 2.7 cm) has been selected to reduce NH_3 decomposition at high temperature and the presence of water as a reaction product. Also small amounts of $AlPO_4$ precursor (60 mg) are preferred to lower the reaction time. Nitridation was found to be negligible below 650 °C. Above 800 °C phosphorus is eliminated as PH_3 and AlN starts to form. Thus the temperature range in which nitridation occurs is between 650 and 800 °C, with P/Al = 1 and $2N^{3-}/3O^{2-}$ stoichiometry. Nitridation times of 1.5, 2, 4, 7, 18 and 60 h were selected to obtain 2.8, 3.6, 7.2, 11, 17.5 and saturation 20 mass% N respectively. Nitrogen content was determined by alkaline digestion with molten KOH at 400 °C and resulting NH_3 titration with H_2SO_4. Non-crystallinity of AlPON samples was checked by XRD.

Amorphous $AlPO_4$ precursor was previously synthesised by mixing, at room temperature (RT) for 1 h two aqueous solutions of aluminium nitrate and ammonium dihydrogenphosphate of the same molarity (0.66 M). An excess of citric acid was added and the mixture kept at RT overnight under continuous stirring. The solution was transferred to an evaporating dish and pumped out at 40 °C until water was completely eliminated. The solid was oven-dried at 110 °C overnight and calcined at 500 °C for 20 h.

Analysis techniques

X-Ray photoelectron spectra (XPS) were collected in a Vacuum Generator 210 spectrometer equipped with a hemispherical analyser working at 30 eV constant pass energy. Mg-Kα at 240 W is used as excitation radiation and every spectrum is the result of accumulating 10 runs at 0.1 eV steps. Samples were evacuated overnight at RT in a preparation chamber (5×10^{-8} Torr base pressure). C 1s, Al 2s, Al 2p, P 2s, P 2p, O 1s, O KVV and N 1s regions were analysed and quantitative analysis was performed employing sensitivity factors and software provided by the manufacturer. The baseline was subtracted with a Shirley algorithm and peak positions were corrected using residual carbon C 1s binding energy at 284.6 eV.

Diffuse reflectance IR Fourier transform (DRIFTS) spectra were collected in a FT Nicolet 510P spectrometer using a deuterated triglycine sulfate (DTGS) detector working at 4 cm^{-1} resolution. The sample was placed inside a controlled environment chamber (Spectra-Tech 0030–101) attached to a diffuse reflectance accessory (Spectra-Tech Collector). Undiluted AlPON solids were heated at 500 °C for 1 h under continuous nitrogen flow (50 ml min^{-1}). One hundred scans were accumulated and data presented in absorbance mode after a 9 points–3 passes Savitzky–Golay smoothing treatment. Powdered KBr was employed as background.

Results

X-Ray photoelectron spectroscopy

Al 2s, Al 2p, P 2s, P 2p, O 1s, O KVV and N 1s regions has been analysed for the entire AlPON series. Peak positions, referred to C 1s at 284.6 eV, *vs.* nitrogen content are compiled in Table 1. As can be observed, the progressive nitridation of aluminophosphate causes a systematic decrease in binding energy for Al, P, O and N levels.

Regarding the peak shape, Al, P and O peaks are quite symmetric, however N 1s shows some asymmetry on the high E_b side, Fig. 1. Unfortunately, it is not possible to discriminate between >N—, =N— and —NH— groups.[13,14] Indeed, the N 1s peak can be described as the sum of two components (A and B). The high energy component (398.9 eV) dominates the spectra at low nitrogen content (below 5%) but the low energy contribution (397.5 eV) rapidly takes over as the nitrogen concentration increases. The displacement of the N 1s signal is not a real energy shift but a convolution effect due to a modification in the relative proportions of these two peaks. Areas of both components are calculated and plotted *vs.* mass% N. The contribution at 397.5 eV increases parallel to the nitrogen content while the high binding energy peak remains essentially constant. Based on this, we assign the peak at 397.5 eV to structural nitrogen (>N—, =N—, or —NH—). The weak 398.9 eV signal is due to terminal —NH_2 groups.

Table 1 Binding energy values (eV) referred to C 1s (284.6 eV) for the AlPON series as a function of their nitrogen content. γ-Al_2O_3 and phosphorus oxynitride (PON) are also included

	E_b/eV					
mass% N	Al 2s	Al 2p	P 2s	P 2p	O 1s	N 1s
0	119.5	74.6	191.6	134.3	532.2	—
2.8	119.4	74.5	191.5	134.3	532.2	398.9
3.6	119.2	74.4	191.3	134.0	532.3	398.9
7.2	119.4	74.5	191.3	133.9	531.9	398.1
11	119.2	74.3	191.0	133.6	531.8	397.7
17.5	118.9	73.9	190.5	133.0	531.7	397.5
20	118.7	73.7	190.3	132.7	531.2	397.5
γ-Al_2O_3	118.8	74.0	—	—	530.9	—
PON	—	—	192.4	135.1	534.4	398.8

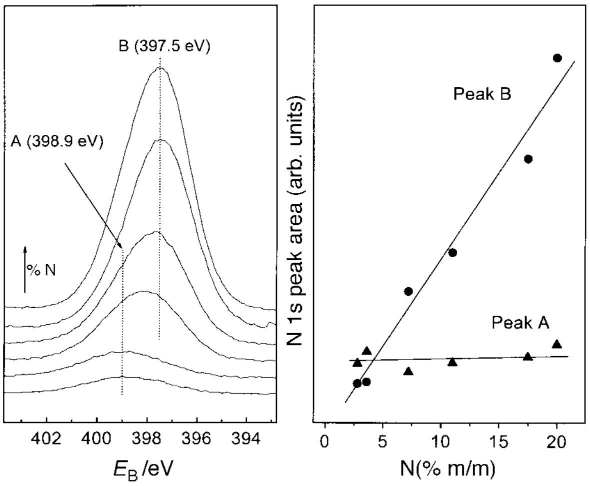

Fig. 1 Contribution of components at 397.5 eV and 398.9 eV to the N 1s XPS peak of AlPON as a function of nitrogen percentage. Intensities have been corrected with surface specific area.

In a previous paper we have observed a modification in the separation between the $KL_{23}L_{23}$ and the KL_1L_{23} levels from the O KVV spectra in aluminophosphate solids with a variable P/Al ratio.[15] This phenomenon is related with a modification in the ionic character of the P—O bonds[16] caused by the substitution of P by Al. However, in the AlPON series, the $KL_{23}L_{23}$–KL_1L_{23} separation is 21.6 ± 0.2 eV despite the nitrogen load. This should be understood as a non-modification of the bonding characteristics at oxygen in a short range. The shift of binding energies values for O 1s (Table 1) is then due to a long range interaction caused by a modified framework in which oxygen is being replaced by nitrogen.

FWHM (full width half maximum) values for Al 2s, Al 2p, P 2s, P 2p and O 1s are summarised in Table 2 and very differentiated behaviour is observed: while Al peaks follow a decreasing trend, P levels show a mild maximum and O 1s remains constant. Such a difference between P and Al agrees with the hypothesis that nitrogen replaces oxygen by bonding selectively to P rather than to Al.[2] Our interpretation of these results is that the incorporation of nitrogen to the $AlPO_4$ framework creates a variety of P short range environments leading to a broadening in the XPS peaks. Such a variety is maximum around 10–12 mass% N, Table 2. Above 17 mass% N a strong definition of the P short range environment appears causing the narrowing of P peaks. However, the definition of Al environment is progressive, even from the early stages of $AlPO_4$ nitridation.

From the areas of XPS peaks and tabulated sensitivity factors we can obtain the surface compositions of AlPON samples, Table 3. Compared to theoretical bulk values (*i.e.*

Table 2 Full width at half maximum values for XPS peaks of AlPON and γ-Al_2O_3

	FWHM/eV					
mass% N	Al 2s	Al 2p	P 2s	P 2p	O 1s	N 1s
0	3.12	2.81	3.54	2.76	2.87	—
2.8	3.11	2.85	3.60	2.83	2.99	3.80
3.6	3.04	2.78	3.59	2.85	2.87	3.84
7.2	2.94	2.64	3.61	2.89	2.83	3.51
11	2.91	2.65	3.62	2.90	2.86	3.37
17.5	2.96	2.73	3.52	2.83	2.99	3.23
20	2.67	2.36	3.15	2.60	2.89	3.11
γ-Al_2O_3	2.70	2.35	—	—	2.92	—

Table 3 Surface composition obtained from XPS for AlPON samples

	atom%			
mass% N	Al	P	O	N
0	14.9	13.9	71.2	0
2.8	15.5	12.8	68.6	3.1
3.6	14.3	14.3	67.0	4.4
7.3	13.8	15.4	60.3	10.5
11	14.0	15.5	54.4	16.1
17.5	15.5	14.9	44.5	25.1
20	14.9	15.9	36.7	32.5

assuming P/Al = 1 and isoelectronic substitution 3 O^{2-}/2 N^{3-}) XPS analysis underestimates Al and P concentration by *ca.* 15–20% and overestimates oxygen content by 10–15% at the surface. Discrepancies are easily explained by the presence of residual adsorbed water that increases the percentage of oxygen and therefore decreases the remaining elements. However, nitrogen theoretical bulk composition and surface percentages obtained by XPS correlate quite well, Fig. 2. Such a good agreement from predicted bulk and surface compositions indicates a high compositional homogeneity in AlPON solids and the absence of strong surface segregations. In this particular case and despite its high surface sensitivity, XPS is a suitable technique for bulk AlPON analysis and quantification.

Diffuse reflectance Fourier Transform IR spectrsocopy (DRIFTS)

DRIFTS spectra obtained at 500 °C under N_2 flow are plotted in Fig. 3. Data are displayed as a function of the mass% N in two regions (4000–2400 and 2300–550 cm^{-1}).

At low nitrogen content, bands at 980 and 760 cm^{-1} are observable. They are assigned to ν_{as} and ν_s of P—O—P bonds, respectively.[17] These bands become weaker until they are replaced by another at 910 cm^{-1} ascribed to ν_{as} in P—N—P or P—NH—P bonds,[18,19] as expected from progressive oxygen substitution by nitrogen in AlPON materials.

The main peak in the 2300–550 cm^{-1} range is located between 1350 and 1280 cm^{-1}. It becomes broader and shifts to lower wavenumbers as the mass% N is raised. P=O and $-PO_2$ (in C_{2v} symmetry) stretchings occur in this frequency range[17,20,21] and band broadening can be explained by a growing contribution of P=N (—N=P—N=) bonds in cyclic ring structures (1315–1218 cm^{-1})[22] overlapping the P—O stretching. The hypothesis of cyclic ring structures with alternating P—N—P bonds is reinforced by the presence, at high nitrogen percentages, of a broad and weak band around 2700 cm^{-1} that is associated to hydroxy groups linked to P in P—N—P bonds in cyclic phosphonitrilates.[18]

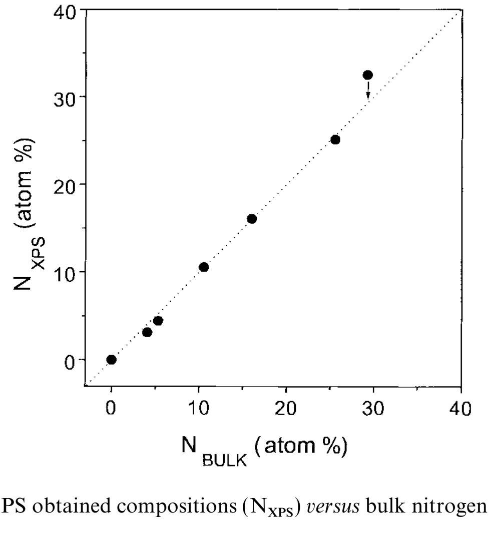

Fig. 2 XPS obtained compositions (N_{XPS}) *versus* bulk nitrogen content

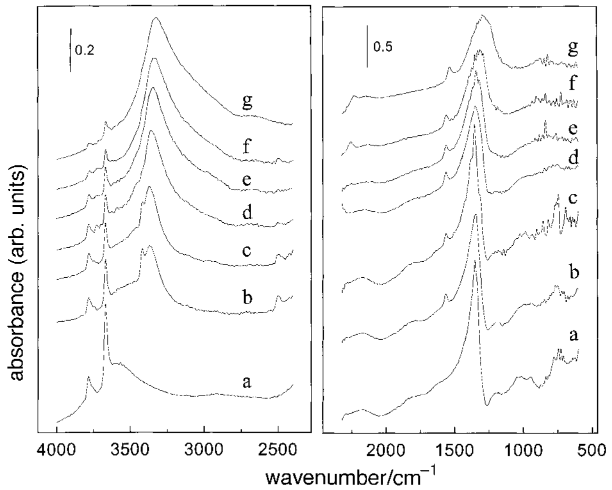

Fig. 3 DRIFTS spectra at 500 °C under nitrogen flow of AlPON materials with variable nitrogen percentage: (a) 0%, (b) 2.8%, (c) 3.6%, (d) 7.2%, (e) 11%, (f) 17.5% and (g) 20% (m/m)

The shift to lower frequencies can also be due to P=N contributions or simply the influence of the lower electronegativity of nitrogen replacing oxygen linked to P.[23,24] A similar frequency displacement was also observed by Steger and Lunkwitz when comparing cyclic imidophosphates and the corresponding isoelectronic cyclic metaphosphates.[19]

A characteristic feature of AlPON with respect to $AlPO_4$, is the presence, even at very low nitrogen doses, of a sharp peak at 1560 cm^{-1} caused by terminal $-NH_2$ groups associated with phosphorus.[25]

A band at 2250 cm^{-1} develops at high nitrogen content. We assign this new feature to P—H stretching in terminal $-PH_2$ groups. AlPON solids are found to yield gaseous PH_3 above 500 °C.[26] Generation of $-PH_2$ groups can then be considered as the preliminary stage of PH_3 formation.

The 4000–2400 cm^{-1} region in AlPON materials, Fig. 3, is progressively dominated by a strong band at 3350 cm^{-1} caused by structural (N—H) stretchings.[25] Well defined peaks at 3785 and 3670 cm^{-1} are respectively assigned to hydroxy groups bonded to Al and P in tetrahedral coordination. It is also possible to detect hydroxy groups bonded to Al cations in an octahedral environment (3725–3730 cm^{-1})[27–29] especially at moderate nitrogen percentages. Even a pentahedral [AlO_5] group is observable (shoulder at 3750 cm^{-1})[30] at low nitrogen content.

The minor presence of a hydrated phosphate phase is postulated at low nitrogen percentage from a weak but sharp hydroxy peak at 3420 cm^{-1}.[17] Under the same conditions, hydroxy groups associated to terminal —P=O are also observable (weak peak at 2500 cm^{-1}).

Discussion

The starting point on the study of the short range structure of amorphous aluminophosphate oxynitrides (AlPON) is to consider them as isostructural with the amorphous $AlPO_4$ precursor. AlPON is then built up of alternating [PO_4] and [AlO_4] tetrahedra in which oxygen has been partially replaced by nitrogen according to the ratio $3O^{2-}/2N^{3-}$.

There are many results from ^{27}Al, ^{31}P NMR, XPS and IR pointing to the selective replacement of oxygen bonded to phosphorus. Besides, no direct Al—N bonds have been described.[2,31–33] Preference of N for P is based on the enhanced strength of P—N and Al—O bonds with respect to P—O and Al—N.[31] The same conclusion can be deduced from our XPS results. The narrowing in Al peaks suggests the progressive formation of a well defined (Al—O) phase while the broadening and further narrowing of P peaks indicates the formation of a mixture of [$PO_{4-x}N_x$] units.

The formation of a new (Al–O) phase, tentatively Al_2O_3-like, is supported by other experimental results. For instance, the progressive evolution of E_b and FWHM values for Al 2s, Al 2p and O 1s towards those obtained in the same instrument and conditions for γ-Al_2O_3, Tables 1 and 2. Also DRIFTS reveals a structural modification in the O—H stretching of hydroxy groups linked to Al, Fig. 3. In order to better characterise those changes, the 3850–3600 cm^{-1} region has been expanded and normalised in Fig. 4. In $AlPO_4$ only tetrahedral [AlO_4] and some pentahedral [AlO_5] units are observable. As nitridation progresses, [AlO_5] polyhedra start to develop at low nitrogen content and later [AlO_6] octahedra are defined. The disappearance of hydroxy groups attached to phosphorus is faster than that of hydroxy groups linked to Al cations {[AlO_x]$_{tot}$/[P(O,N)$_4$]}. This is indicative of the selective removal of oxygen from the phosphorus coordination sphere. Meanwhile the amount of octahedrally coordinated Al grows {[AlO_6]/[AlO_x]$_{tot}$}, as expected from the segregation of a γ-Al_2O_3 type phase.[34] It is interesting that the transformation of [AlO_4] polyhedra into [AlO_6] seems to go *via* a [AlO_5] intermediate {[AlO_5]/[AlO_x]$_{tot}$ ratio in Fig. 4}.

Finally, *ab initio* calculations on amorphous AlPO systems with a variable P/Al ratio predict an structure based on metaphosphate ions connected by layers of an Al-rich phase resembling γ-Al_2O_3.[11]

Models for nitrogen incorporation to metaphosphates (MPO_3) described the formation of [PO_3N] and [PO_2N_2] polyhedra but discarded the possibility of obtaining [PON_3] units.[14,33,35] Indeed [PO_3N], [PO_2N_2] and even [PN_4], but no [PON_3], polyhedra have been experimentally detected.[36,37] Actually, the formation of [PON_3] is the limit for the amount of nitrogen that can be introduced in metaphosphates. In aluminophosphate oxynitrides (AlPON), the limit is the ($AlPON_2$) composition[38] which gives a theoretical 27.5 mass% N. Such a nitrogen content cannot be experimentally achieved without the formation of some AlN.[38] Preliminary EXAFS results in our nitrogen saturated AlPON sample (20 mass% N) reveal that the number of N and O atoms surrounding P is two.[39] The bulk structure can then be described as a network of [PO_2N_2] polyhedra. [PO_2N_2] are also the building units of phosphorus oxynitrides (PON).[40] However, (PON) binding energy values do not match with those of AlPON (20 mass% N), Table 1. Discrepancies can be due to the contribution of the (Al–O) phase to the framework potential in AlPON, as also suggests the non-modification of the $KL_{23}L_{23}$–KL_1L_{23} separation. However, the possibility of a non-correspondence between the structure of PON and AlPON is still open to discussion.

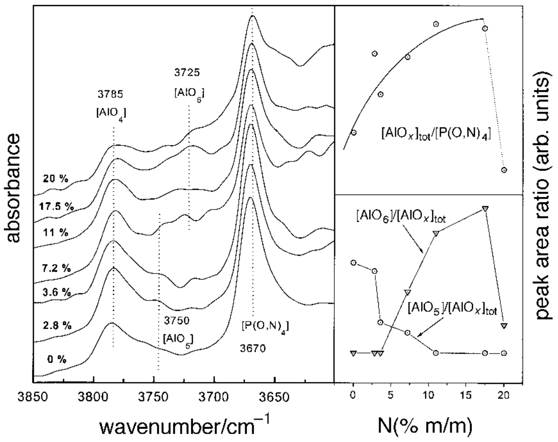

Fig. 4 Expanded 3850–3600 cm^{-1} DRIFTS region of AlPON as a function of the nitrogen content. For clarity, intensities are normalised. Ratios between peak areas are included on the right.

Binding energy values in the nitrogen saturated AlPON sample are very similar to those of phosphorus nitride (P_3N_5).[41] A hypothetical mixture $Al_2O_3 + P_3N_5$ with P/Al=1 would be 22.2 mass% N) in nitrogen, in good agreement with the experimental saturation value (20 mass% N). Atomic percentages would be Al (19.4%), P (19.4%), O (29%) and N (32.3%), which are also very similar to the experimental values, Table 3. The presence of bulk P_3N_5 made up of [PN_4] tetrahedra is discarded from EXAFS results.[39] However, the formation of a $Al_2O_3 + P_3N_5$ mixture at the surface of nitrogen saturated AlPON would explain XPS data without contradicting EXAFS owing to the enhanced surface sensitivity of XPS. Indeed, the slight enrichment in N found at 20 mass% N, compared with the theoretical value, Fig. 2, would be consistent with the presence of such a surface P_3N_5 phase.

Despite the bulk character of IR, DRIFTS has been described to be more sensitive to surface species.[42] A closer look to the hydroxy region, Fig. 4, reveals some drastic changes at the nitrogen saturation dose. For instance, the growing trend for the [AlO_x]$_{tot}$/[P(O,N)$_4$] ratio is suddenly broken, basically caused by the disappearance of octahedrally coordinated Al. The lack of [AlO]$_6$ units is an unexpected result based on the argument about the formation of a γ-Al_2O_3 type phase. However, this result does not mean that octahedral Al is absent, it could merely be due to the non-existence of hydroxy groups linked to Al. Actually the amount of hydroxy groups attached either to Al or P decreases with time of nitridation, Fig. 3. The possibility of diffusion of the γ-Al_2O_3 phase into the bulk is rejected from the surface composition, Table 3.

Another important aspect to analyse in the characterisation of aluminophosphate oxynitrides (AlPON) is to clarify the bonding state of nitrogen. Triply (>N—) (399.1 eV) and doubly bonded (397.6 eV) (=N—) nitrogen (to phosphorus) have been identified by XPS in nitrided phosphate glasses.[13,14] However, few reports of —NH— occur for these systems.

The two contributions found in AlPON at 398.9 and 397.5 eV, Fig. 1, could correlate quite well with the above mentioned (>N— and =N—) assignments. However, there are a couple of experimental results on AlPON that are not explained by models applied to nitrided phosphates. First, the most widely accepted nitridation mechanism[43] predicts a constant ratio (=N—)/(>N—)=3. In our samples, the ratio, peak B/peak A, ranges from 0.05 to 8.1 upon increasing the nitrogen content, Fig. 1. Secondly, E_b for structural —NH— reported in the literature[44] is between 399 and 400 eV. Based on this, no —NH— groups should be observable in AlPON. However, the presence of a very intense and growing band at 3350 cm^{-1}, Fig. 3, is a strong experimental support for the existence of N—H bonds. The assignment of this band to N—H stretching in terminal —NH_2 groups is discarded by comparison with the intensity of the other band characterising —NH_2 groups at 1560 cm^{-1}. Besides, the replacement of oxygen by isoelectronic —NH— has been proposed in the thermal ammonolysis of $AlPO_4$–5 molecular sieves.[31]

Comparing both XPS and DRIFTS spectra, the high binding energy peak (398.9 eV) is ascribed to terminal —NH_2 based on its constancy *vs.* nitrogen content (intensities of peak at 1560 cm^{-1} in Fig. 3 and peak A in Fig. 1). The more intense peak at 397.5 eV is then due to structural nitrogen (—NH—, >N— and =N—). From these results we propose that nitridation of $AlPO_4$ starts at the surface, breaking P—O—P bonds to give terminal P—NH_2. Once P—NH_2 saturation coverage is reached bulk nitridation starts.

DRIFTS spectra, Fig. 3, provide some indications about the presence of cyclic structures in AlPON materials. For instance, the shift towards lower frequencies of the main band can be due to the contribution of P—N stretchings (1315–1218 $\mathrm{cm^{-1}}$) in alternating cyclic arrangement ($-\mathrm{N}{=}\mathrm{P}{-}\mathrm{N}{=}$)[22] or just the same effect observed by comparing cyclic imidophosphates and the corresponding cyclic metaphosphates.[19] Also a weak and broad band around 2700 $\mathrm{cm^{-1}}$ can be associated with hydroxy groups bonded to P in the above referred ($-\mathrm{N}{=}\mathrm{P}{-}\mathrm{N}{=}$) cyclic arrangement.[18] For this reason-modelling of AlPON structure based on cyclic clusters and *ab initio* calculations on them is a reasonable alternative to complement experimental results.

Conclusions

The establishment of the short range structure of aluminophosphate oxynitride (AlPONs) is difficult owing to their amorphous character. However, characterisation techniques such as XPS and DRIFTS are capable of detecting the selective nitridation of phosphorus and the progressive formation of an $\mathrm{Al_2O_3}$-type phase. Experimental results are also consistent with the build up of a surface $\mathrm{P_3N_5}$ phase in nitrogen saturated AlPON materials. It is not possible to discriminate between doubly ($=\mathrm{N}-$) and triply ($>\mathrm{N}-$) nitrogen bonded to phosphorus, but the presence of ($-\mathrm{NH}-$) is clear from DRIFTS spectra. Nitridation of $\mathrm{AlPO_4}$ starts at the surface forming $\mathrm{P{-}NH_2}$ until saturation coverage is achieved with no bulk nitridation being observed prior to this. Finally, the presence of cyclic structures containing alternating (P—N—P) bonds is presumed from DRIFTS data and the AlPON structure is proposed as a network of such cyclic clusters linked through an $\mathrm{Al_2O_3}$-type phase. *Ab initio* calculations on this model are currently under progress to complement experimental results.

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