

DRIFTS Study of the Surface Structure and Nitridation Process of Mixed Galloaluminophosphate Oxynitride (AlGaPON) Catalysts

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The spectra of high surface area amorphous oxide AlPO, AlGaPO, and GaPO were compared with those of high surface amorphous oxynitrides AlPON and AlGaPON with similar O/N ratio and with that of the nitride GaN. This allowed us to make a correct assignation of the bands in their IR vibrational spectra, especially those in the new family of solids named galloaluminophosphate oxynitride, AlGaPON. The substitution of aluminum atoms by gallium induces a shift of the framework band vibrations due to a second-neighbor effect. The introduction of nitrogen in the network of the oxide phosphate produces a broadening and poor definition of the structural bands due to a collapse of the structure. NH_4^+ , coordinated NH_3 , $-\text{NH}_2$, and $-\text{NH}-$ species are identified on the surface of the AlGaPON solid. A thermal treatment under NH_3 allows us to propose the following nitridation sequence: $\text{M}-\text{O}-\text{NH}_4^+$ and/or $\text{M}-\text{NH}_3 \rightarrow \text{M}-\text{NH}_2 \rightarrow \text{M}-\text{NH}-\text{M} \rightarrow \text{N}^{3-}$.

Introduction

We have recently reported that it is possible to substitute part of the oxygen atoms by nitrogen in amorphous aluminophosphate by thermal activation under ammonia flow.^{1–4} The resulting high surface area amorphous oxynitride solid, named “AlPON”, presents basic properties and has been successfully used as a solid base catalyst and support.^{2,3,5–11}

The same method of synthesis has also been successfully used to prepare other oxynitride systems, such as zirconophosphate oxynitrides (ZrPON),^{12–14} aluminovanadate oxynitrides (VAION),^{15–18} and galloaluminophosphate oxynitrides (AlGaPON).^{19–21} The amount of nitrogen incorporated to the oxynitride may be adjusted during the synthesis and depends on the experimental conditions (nitridation temperature, ammonia flow, contact time, etc.).^{1,18,19} As the surface basicity of all the oxynitrides increases with the nitrogen content, solids with designed acid–base properties may be prepared. It is then mandatory to identify the nature of the nitrogen surface species in order to understand the role of nitrogen in the formation of these acid–basic sites.

FT-IR spectroscopy is a very used and powerful nondestructive characterization technique that provides information about the vibrational structure of the samples and is ideal for identifying functional groups, reactive sites, and adsorbed species on the surface of the solids. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), besides the ease of preparation, allows us to obtain the IR spectrum of a sample in its original form, without any treatment or dilution. In addition, the higher sensitivity to surface species compared with the transmission IR technique and its capacity to control the environmental conditions (temperature, pressure, and atmosphere) has made it a tool much used in surface chemistry.²²

and which was successfully used to characterize oxynitride systems.^{6,7,23–31}

The aim of the paper is to state the vibrational spectrum of galloaluminophosphate oxynitrides and give some clues about the nitridation mechanism.

This paper reports a DRIFTS study of the surface structure, thermal stability, and thermal treatment under NH_3 of a galloaluminophosphate oxynitride. To assign the vibrations in the AlGaPON solid correctly, a comparison with the results obtained on the oxide precursor, AlGaPO, the monometallic phosphates, AlPO and GaPO, the oxynitride AlPON, and the gallium nitride GaN is proposed.

Experimental Section

A high surface area amorphous aluminophosphate sample (AlPO) was synthesized by the citrate method.³² Two aqueous solutions of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck) and $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ (Merck), with the same molarity, in order to obtain an Al/P ratio of 1, were mixed for 1 h at room temperature (RT) under stirring. Then, an excess of citric acid (Merck) was added and the mixture was kept overnight under continuous stirring. After water evaporation under reduced pressure, the gel obtained was dried for 10 h at 100 °C in a vacuum oven (50 mbar). Finally, the solid was calcined for 16 h at 550 °C and sieved ($100 < \phi < 200 \mu\text{m}$).

High surface area amorphous gallium and mixed galloaluminophosphate samples were prepared by a sol–gel method originally described by Kearby.³³ A solution of the amounts of Ga^{3+} , Al^{3+} , and H_3PO_4 2 M was adequate to obtain a P/Ga ratio of 1 in the case of GaPO solid, and P/(Ga + Al) and a Ga/Al ratio of 1, for AlGaPO, were mixed and cooled to 0 °C with a dry ice/alcohol bath. Then, a large excess of propylene oxide was slowly added under vigorous stirring. After some hours at room temperature, a translucent gel was produced which was washed with 2-propanol and dried at 110 °C. The resulting powder was sieved ($\phi < 100 \mu\text{m}$) and calcined in air at 650 °C.

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TABLE 1: Physical Properties of the Solids

sample	composition	preparation method	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	N content (% w/w)
AlPO	AlPO_4	citrate	316	
AlGaPO	$\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$	Kearby method ^a	238	
GaPO	GaPO_4	Kearby method ^a	280	
AlPON	$\text{AlPO}_{1.71}\text{N}_{1.53}$	NH_3 200 h	195	20
AlGaPON	$\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_{1.81}\text{N}_{1.46}$	NH_3 16 h	145	15.9
GaN	GaN	commercial	<1	16.7

^a See ref 33.

The AlPO and AlGaPO precursors were activated under NH_3 flow (30 L h^{-1}) for 200 h at 800°C and 16 h at 750°C , respectively, to obtain the corresponding oxynitrides. Experimental conditions were selected to obtain almost the same O/N atomic ratio for the oxynitrides.

Commercial GaN (CERAC, 99.9% pure, ($\varnothing = 100 \mu\text{m}$)) was used as received.

The total nitrogen content of the nitrided samples was determined by titration with a sulfuric acid solution of the ammonia liberated by alkaline digestion at 400°C with melted KOH.³⁴

The specific surface area was measured by the single-point BET method in a Micromeritics Flowsorb II 2300 apparatus, after 20 min degassification at 250°C .

In situ diffuse reflectance infrared fourier Transform spectroscopy (DRIFTS) spectra were collected in a Bruker IFS88 infrared spectrometer with KBr optics and a DTGS detector. Pure samples were placed inside a commercial controlled environmental chamber (Spectra-Tech 0030–103) attached to a diffuse reflectance accessory (Spectra-Tech collector). Samples were heated from room temperature to 500 – 600°C under a 30 mL min^{-1} inert gas flow (N_2 or He, L'Air Liquide, 99.999%), obtaining spectra (200 scans, 4 cm^{-1} resolution) every 50 or 100°C after 30 min of stabilization. For the thermal treatment under NH_3 , 30 mL min^{-1} of gaseous NH_3 (3000 ppm in He 99.5%, L'Air Liquide) was flowed through the AlGaPO sample and the temperature was raised from room temperature to 650°C , obtaining spectra as previously mentioned.

Results and Discussion

Physical Properties. Table 1 reports the chemical composition, the specific surface area as well as the bulk nitrogen content of the solids. Since the oxygen content of the samples has not been titrated, the composition of the samples is deduced assuming all phosphorus atoms are forming orthophosphate anions, although the possibility of the existence of metaphosphate anions has been also suggested in amorphous aluminophosphates.²⁷

Vibrational Structure of the Oxide Precursors (AlPO, AlGaPO, and GaPO). Figure 1 shows the “in situ” DRIFTS spectra of the GaPO (a), AlGaPO (b), and AlPO (c) oxide precursors obtained at 200°C .

In the framework vibration region, all three solids present a similar spectra, with five broad bands at about 1300 , 1200 , 1040 , 740 , and 550 cm^{-1} and a narrow one at about 950 cm^{-1} . All these bands have been generally assigned, in AlPO and AlPON samples, to P–O, Al–O, or combinations of P–O and Al–O stretching modes.^{24,30,31,35} However, recent ab initio studies show that it is almost impossible to separate Al–O from P–O

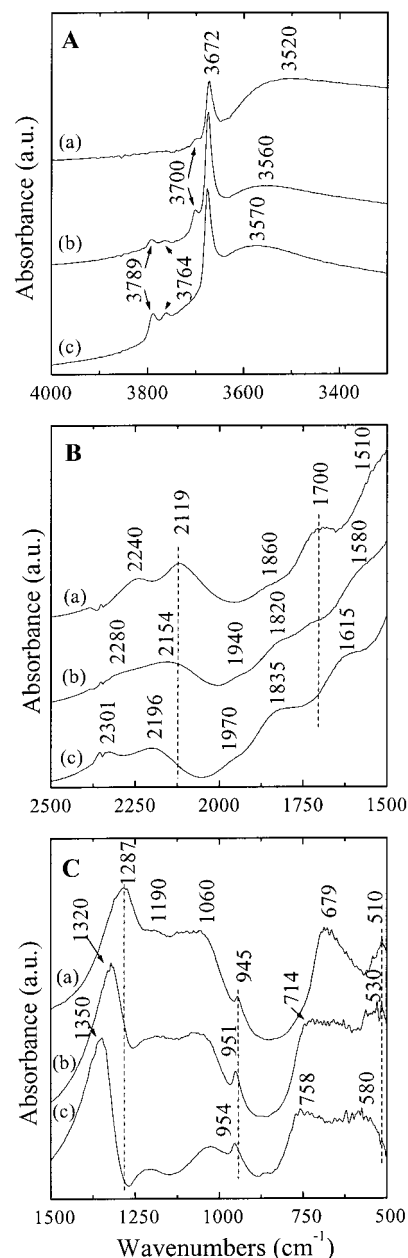


Figure 1. In situ DRIFTS spectra obtained at 200°C of (a) GaPO, (b) AlGaPO, and (c) AlPO samples. For clarity, the spectra are displayed in three regions: (A) 4000 – 3300 cm^{-1} ; (B) 2500 – 1500 cm^{-1} ; (C) 1500 – 500 cm^{-1} .

vibrational modes in amorphous aluminophosphates.²⁷ In that sense, the presence of the same bands in the spectrum of GaPO points to such vibrations being related with the tridimensional network of the solids. Thus, although the complicated structure observed in this region is due to a combination of the overlapped Al–O, Ga–O, and P–O vibration bands, we must assign them essentially to vibrations where phosphorus atoms are implied.

The main feature in this region is a large and intense absorption centered at about 1300 cm^{-1} , assigned to both P=O and $-\text{PO}_2$ stretching vibrations of the solid. This band shifts to lower wavenumbers when the gallium content increases (1350 cm^{-1} , AlPO; 1320 cm^{-1} , AlGaPO; 1287 cm^{-1} , GaPO). The same behavior has been observed in $\gamma\text{-Al}_2\text{O}_3$ doped with lanthanide ions, where the frequency of the main DRIFTS vibration at about 1050 cm^{-1} decreases when the radius of the lanthanide³⁶ increases, and was ascribed to a second-neighbor effect. In our case, the same explanation can be proposed since

TABLE 2: Positions (in cm^{-1}) and Assignments of the DRIFTS Bands Observed in the Spectra at 200 °C of the Oxide Phosphates AlPO, AlGaPO, and GaPO

AlPO	AlGaPO	GaPO	assignments
580	530	510	$\nu(\text{P}-\text{O}-\text{P})$
758	714	679	$\nu_s(\text{P}-\text{O}-\text{P})$
954	951	945	$\delta(\text{OH})$ in tetrahedral P-OH
1030	1040	1060	$\nu_{\text{as}}(\text{P}-\text{O}-\text{P})$
1210	1194	1190	P-O and P-O-P
1350	1320	1287	$\nu(\text{P}=\text{O})$ in P=O
1615	1580	1510	overtones and combinations bands of the lattice vibrations
1835	1820	1700	overtones and combinations bands of the lattice vibrations
1970	1940	1860	overtones and combinations bands of the lattice vibrations
2196	2154	2119	overtones and combinations bands of the lattice vibrations
2301	2280	2240	overtones and combinations bands of the lattice vibrations
3570	3560	3520	$\nu(\text{OH})$ in H-bonded OH
3676	3674	3672	$\nu(\text{OH})$ in tetrahedral P-OH and/or $\nu(\text{OH})$ in Ga-OH
	3700	3700	$\nu(\text{OH})$ in Ga-OH
3764	3767		$\nu(\text{OH})$ in Pentahedral Al-OH
3789	3790		$\nu(\text{OH})$ in Tetrahedral Al-OH

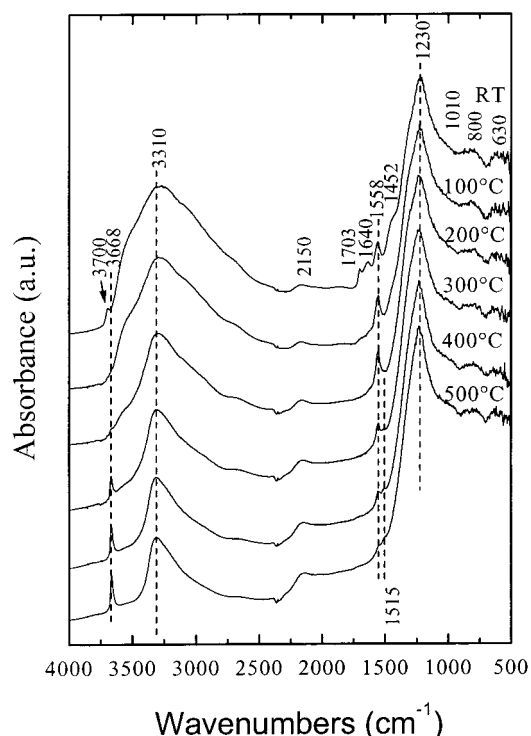
gallium has a higher radius than aluminum, leading to a decrease of the P=O stretching vibration position.

This second-neighbor effect can also be detected in the other vibrations appearing in the framework region. Thus, the bands at 550 and 740 cm^{-1} shift to lower wavenumbers with the Ga content, suggesting that they correspond to vibrations influenced by the Al/Ga substitution. On the contrary, the small shift of the band at 950 cm^{-1} (about 10 cm^{-1}) and its narrowness indicates that this vibration is not much affected by the environment of the lattice. Thus, although in AlPO solids this band has been assigned to Al-O stretching vibration bond³⁵ because of its position very close to that observed for the main peak in Al_2O_3 (960 cm^{-1}),³⁷ we support its assignation to bending modes of free P-OH groups, as proposed for phosphated alumina³⁸ and molecular sieve cloverite³⁹ (GaPO_4) samples. In this later work, the assignation to hydroxyl groups is confirmed by its perturbation with pyridine at room temperature.

Another important feature is the presence of five bands between 2500 and 1500 cm^{-1} . They are attributed to overtones and combinations of the lattice vibrations.^{24,40} This is clearly demonstrated by the shift of these bands with the Ga/Al ratio in the same sense as that observed for the intense P=O vibration band, so that the separation between these bands and the main P=O stretching one remains practically constant from one solid to another.

The comparison of the 4000–2500 cm^{-1} region of the three phosphates allows us to assign the different hydroxyl groups present in the solids. The AlPO solid has bands at 3789, 3764, 3676, and 3570 cm^{-1} , which can be ascribed to hydroxyl coordinated to tetra- and pentahedral aluminum, tetrahedral phosphorus, and bridging OH groups, respectively.^{24,35,41} Besides these bands, the AlGaPO solid presents a new feature at 3700 cm^{-1} which can be assigned to Ga-OH groups.^{40,42} In agreement with these assignments, the vibrational spectrum of the GaPO solid presents only the bands at 3700, 3672, and 3560 cm^{-1} , assigned to hydroxyl groups attached to gallium and phosphorus and H-bonded OH groups.

Table 2 summarizes all the IR band assignments for these solids.

**Figure 2.** In situ DRIFTS spectra of GaN solid as a function of temperature.

Gallium Nitride (GaN) Vibrational Structure. Figure 2 shows the “in situ” DRIFTS spectra of a commercial GaN obtained at the temperatures indicated.

In the framework vibrational region, the spectra are quite different from those observed for the oxide phosphates. GaN presents broad and ill-defined bands with a main broad and intense absorption band at about 1230 cm^{-1} assigned to the stretching vibration of the Ga-N bond. Besides this, very broad bands at 630, 800, and 1010 cm^{-1} are also observed and should also be assigned to Ga-N or combination bands. In this sense, GaN LO and TO phonon modes have been described at 737 and 560 cm^{-1} , respectively.⁴³ As for the precursor oxides, the overtones and/or combinations of these bands are present in the 2300–2000 cm^{-1} region (maximum at 2150 cm^{-1}).

At room temperature, besides the intense bands due to water adsorbed on the surface (1640 cm^{-1} , $\delta(\text{HOH})$; 3500 cm^{-1} , $\nu(\text{OH})$), we can distinguish bands due to hydroxyl-bonded gallium (Ga-OH) groups at 3700 cm^{-1} and bands at 3310, 3070, 2950, 2690, 1703, 1558, and 1452 cm^{-1} . These last bands can be easily assigned to different surface nitrogenous species, by comparison with the position observed for such species in AlN and AlPON solids^{6,7,23–31} Ga-O-NH₄⁺ (3070 cm^{-1} , $\nu_s(\text{NH})$; 2950 and 2690 cm^{-1} , $\nu(\text{NH})$; 1703 cm^{-1} , $\delta_s(\text{HNNH})$; 1452 cm^{-1} , $\delta_{\text{as}}(\text{HNNH})$), Ga-NH₂ (1558 cm^{-1} , $\delta_s(\text{HNNH})$), and Ga-NH-Ga (3310 cm^{-1} , $\nu(\text{NH})$). The presence of NH₃ species adsorbed on Lewis acid sites of the solids cannot be discarded since they are characterized by a bending band at the same position as that for water adsorbed (ca. 1620 cm^{-1}).⁴⁴

Such NH-containing species present on the GaN surface are formed by the hydrolysis reaction of the Ga-N bonds with the atmospheric water. A similar hydrolysis reaction has also been described for AlN^{45,46} and AlPON solids.^{24,28}

Heating at 200 °C produces the desorption of adsorbed water and ammonium ions. After such temperature, Ga-NH₂ and Ga-NH-Ga are the only nitrogenous species that remain on the GaN surface. In this sense, a shoulder at about 3460 cm^{-1} , which

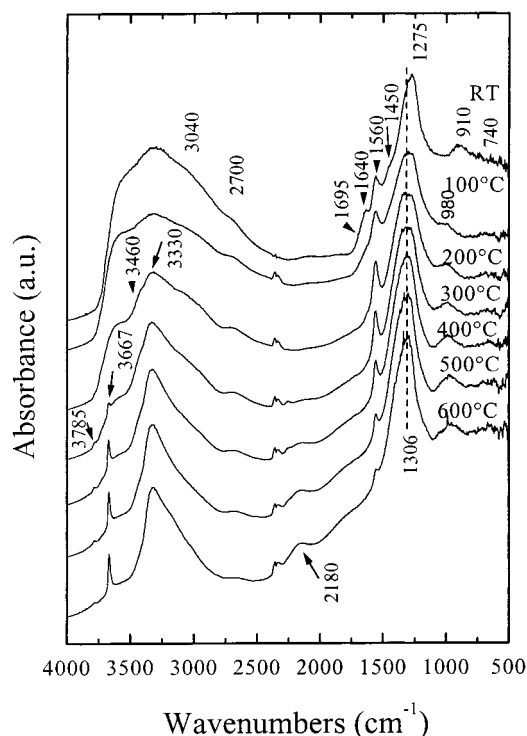


Figure 3. In situ DRIFTS spectra of AIPON solid as a function of temperature.

can be attributed to $\nu(\text{NH})$ in $\text{M}-\text{NH}_2$ species,^{24,28} becomes visible. Moreover, the $\text{Ga}-\text{NH}_2$ band at 1558 cm^{-1} decreases in intensity and, simultaneously, a new one at 1515 cm^{-1} begins to grow. This band can be assigned to $\text{Ga}-\text{NH}_2$ species bridge-bonded to the surface, by comparison with results obtained on AlN ³⁷ and for NH_3 dosed on saturated TM-Al-derived alumina.⁴⁷

It is interesting to note that the surface nitrogenous species attached to gallium present IR bands at the same wavenumbers as reported for those attached to aluminum or phosphorus.^{7,23,24,28,30}

In the hydroxyl stretching region, the intensity of the $\text{Ga}-\text{OH}$ band at 3700 cm^{-1} decreases with temperature and one is developed at 3668 cm^{-1} . This band must be also assigned to $\text{Ga}-\text{OH}$ groups. Indeed, for Ga_2O_3 supported on H-ZSM-5, two hydroxyls bands at 3640 and 3660 cm^{-1} were observed.⁴⁸ In the same sense, for $\text{Ga}-\text{OH}$ groups of extraframework gallium oxide species in $\text{Ga}-\text{ZSM-5}$, two adsorption bands are found at 3670 and 3700 cm^{-1} .⁴² The position of this band coincides with that of the hydroxyl groups attached to tetrahedral phosphorus (see above). This can lead to an erroneous ascription. In fact, two hydroxyl group bands are commonly reported in GaPO_4 solids, one at 3668 cm^{-1} and the other at 3700 cm^{-1} . Although the different authors do not agree on the assignation of the one at 3700 cm^{-1} to $\text{P}-\text{OH}$ ^{49,50} or $\text{Ga}-\text{OH}$ ^{39,40} groups, all of them assign the one at 3668 cm^{-1} to $\text{P}-\text{OH}$ groups.^{39,40,49-51} From the results shown above, we propose the band at 3700 cm^{-1} as due to $\text{Ga}-\text{OH}$ groups and the one at 3668 cm^{-1} as due to both $\text{P}-\text{OH}$ and $\text{Ga}-\text{OH}$ groups.

Aluminophosphate Oxynitride (AIPON) Vibrational Structure. Figure 3 shows the evolution with temperature of the DRIFTS spectra of the AIPON sample.

The main feature of the spectrum at RT is the broad and intense band centered at about 1275 cm^{-1} due to the overlapped $\text{P}=\text{O}$, PO_2 , and $\text{P}=\text{N}$ stretching vibration bands. The shift to lower wavenumbers with respect to the band position in the

precursor AlPO sample (1350 cm^{-1}) is attributed to the substitution of part of the oxygen atoms of the framework of the solid by nitrogen, which presents a lower electronegativity, and by the creation of $\text{P}=\text{N}$ bonds, which have a lower stretching vibration than those of $\text{P}=\text{O}$,²⁸ but not far enough to be distinguished, this causing also a broadening of the band. The framework region, as in the case of GaN , is characterized by very broad and not defined bands, pointing to the partial destruction of the oxide phosphate network, and its replacement by a nitrogen environment. In this sense, the broad band observed at RT at about 910 cm^{-1} has been ascribed to ν_{as} in $\text{P}-\text{N}-\text{P}$ or $\text{P}-\text{NH}-\text{P}$ bonds of AIPON solids,²³ and those at 740 and 980 cm^{-1} observed at high temperatures could be related to $\text{Al}-\text{N}$ LO and TO phonon modes.^{37,46}

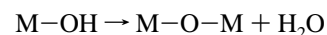
Besides the intense bands due to water adsorbed on the AIPON surface (3590 cm^{-1} , $\nu(\text{OH})$; 1640 cm^{-1} , $\delta(\text{HOH})$), features at 3040 , 2700 , 1695 , 1560 , and 1450 cm^{-1} are observed. They are attributed to NH stretching modes of ammonium ions (3040 and 2700 cm^{-1}) and bending vibrational modes of $\text{H}-\text{N}-\text{H}$ in metal-coordinated NH_2 (1560 cm^{-1}) and NH_4^+ species (1695 cm^{-1} , 1450 cm^{-1}). As said previously, the position of these nitrogenous species bands coincides with those observed in AlN and GaN samples. So, although their assignation to nitrogenous species attached to phosphorus or aluminum is clear, it is not possible to distinguish which is the metal atom that coordinates them.

When increasing the temperature, bands at 1695 , 1640 , and 1450 and the broad feature in the $4000-3000\text{ cm}^{-1}$ range disappear, pointing to the desorption of adsorbed water and ammonium ions from the surface.

The surface cleaning produces a shift in the main band position from 1275 to 1306 cm^{-1} , usually attributed to the loss of nitrogen species²⁸ and an increase in its intensity. Coupled with this, the group of bands in the $2300-2000\text{ cm}^{-1}$ region becomes visible. An intense discussion about the assignation of these bands in AlN , SiN , AIPON, and VAION oxynitrides solids has been reported in the literature. Metal hydride ($\text{M}-\text{H}$) stretching vibration,^{23,52,53} metal dinitrogen ($\text{N}=\text{N}$) stretching vibration,^{18,37,54} and overtones and combination bands of the lattice vibrations^{24,40} have been claimed to be responsible for these bands. Their appearance connected with the intensity increase of the mainframework vibration, besides their presence in all three oxide phosphates considered above (AlPO , AlGaPO , and GaPO), allows us to assign them to overtones and combinations bands of the framework vibrations.

On the other hand, in the OH and NH stretching vibration region, some features at 3785 , 3667 , 3460 , and 3330 cm^{-1} appear. Those at 3460 and 3330 cm^{-1} are assigned to the NH stretching vibration of $\text{M}-\text{NH}_2$ and structural $-\text{NH}-$ groups^{28,55} and those at 3785 and 3667 cm^{-1} to hydroxyl groups bonded to tetrahedral aluminum and tetrahedral phosphorus, respectively. The intensity of the band of $\text{P}-\text{OH}$ groups at 3667 cm^{-1} increases with temperature from 300°C .

On the other hand, above 300°C , the band assigned to $\text{M}-\text{NH}_2$ at 1560 cm^{-1} begins to decrease. This behavior has been related to hydrolysis of the $\text{P}-\text{NH}_2$ groups with water coming from the hydroxyls condensation:^{23,26,28}



this also explains the increase in the number of $\text{P}-\text{OH}$ groups observed at such temperature.

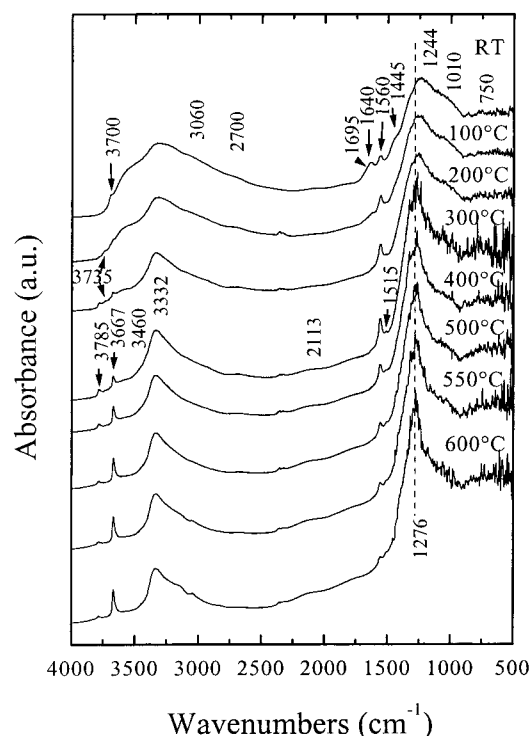


Figure 4. In situ DRIFTS spectra of AlGaPON solid as a function of temperature.

Mixed Galloaluminophosphate Oxynitride (AlGaPON) Vibrational Structure. Figure 4 shows the in situ DRIFTS spectra of the AlGaPON sample as a function of temperature.

At RT, the framework region is characterized by the presence of a broad and intense absorption at 1244 cm^{-1} and ill-defined ones at about 1010 and 750 cm^{-1} . Again, as in the case of the AIPON solid, the spectra in such region do not show the defined bands observed in the oxide phosphates, suggesting the effective introduction of nitrogen in the oxide network. The very complex main band is produced by the overlapped vibrations of P=O , PO_2 , P=N , and Ga-N bonds. As for AIPON, the shift observed to lower wavenumbers, compared to the position observed in the precursor oxide, is associated with the replacement of oxygen by nitrogen. In the same way, as stated for the comparison between AlPO , AlGaPO , and GaPO solids, the presence of gallium produces a shift of the P=O vibration band to lower wavenumbers due to a second-neighbor effect. This explains the shift observed in this band (1244 cm^{-1}) compared with the AIPON sample (1275 cm^{-1}).

As for the AIPON solid, this band increases in intensity and shifts to higher wavenumbers when increasing the temperature (from 1244 to 1276 cm^{-1}). The shift in the position can be related to the nitrogen loss during heating. In this sense, although at room-temperature NH_4^+ (1445 and 1695 cm^{-1}) and NH_2 species [free (1560 cm^{-1}) and H-bonded (1515 cm^{-1})] are detected, ammonium species desorb at 100°C and M-NH_2 species decrease in intensity from 300°C . A shoulder at 3460 cm^{-1} due to $\nu(\text{NH})$ of M-NH_2 groups and another intense band at 3332 cm^{-1} due to structural $-\text{NH}-$ stretching vibrations is also observed; its intensity does not change with the thermal treatment.

The bands due to nitrogenous species present on the AlGaPON surface appear in the same position as those of AlN , GaN , and AIPON solids. Thus, it is impossible to deduce the nature of the metal to which they are attached. Only $-\text{NH}-$ bonds present a light shift to higher wavenumbers as compared with their position in the GaN sample (3310 to 3332 cm^{-1}).

TABLE 3: Positions (in cm^{-1}) and Assignments of the DRIFTS Bands Observed in the Spectra of AIPON, AlGaPON, and GaN Solids

AIPON	AlGaPON	GaN	assignments
		630	Ga-N TO phonon mode
740	750		Al-N TO phonon mode
		800	Ga-N LO phonon mode
910			$\nu_{\text{as}}(\text{P-N-P})$, $\nu_{\text{as}}(\text{P-NH-P})$
980			Al-N LO phonon mode
	1010	1010	Ga-N stretching vibration
		1230	Ga-N stretching vibration
1306	1276		P=O , P-O_2 , P-N , Ga-N stretching vibrations
1450	1445	1452	$\delta_{\text{as}}(\text{HNN})$ in $\text{M-O}^-\text{NH}_4^+$
	1515	1515	$\delta_{\text{s}}(\text{HNN})$ in H-bonded M-NH_2
1560	1560	1558	$\delta_{\text{s}}(\text{HNN})$ in free M-NH_2
1640	1640	1640	$\delta(\text{HOH})$ of adsorbed water
1695	1695	1703	$\delta_{\text{s}}(\text{HNN})$ in $\text{M-O}^-\text{NH}_4^+$
2180	2113	2150	overtone + combination bands of lattice vibrations
2260			overtone + combination bands of lattice vibrations
2700	2700	2690	$\nu(\text{NH})$ in NH_4^+
3040	3060	3070	$\nu(\text{NH})$ in NH_4^+
3330	3332	3310	$\nu(\text{NH})$ in M-NH-M
3460	3460	3460	$\nu(\text{NH})$ in M-NH_2
3590	3560	3570	$\nu(\text{OH})$ in H-bonded OH
3667	3667	3668	$\nu(\text{OH})$ in tetrahedral P-OH and or Ga-OH
	3700	3700	$\nu(\text{OH})$ in Ga-OH
	3735		$\nu(\text{OH})$ in octahedral Al-OH
3785	3785		$\nu(\text{OH})$ in tetrahedral Al-OH

Although this band is too large for an exact determination of its position, and as we have not evidenced a shift when comparing AlGaPON with the AIPON solid, we must relate this shift with a second-neighbor effect due to the presence of gallium atoms, thus also indicating the structural character of the $-\text{NH}-$ groups responsible for such a vibration.

Ga-OH (3700 and 3667 cm^{-1}), tetrahedral P-OH (3667 cm^{-1}), and tetrahedral Al-OH groups (3785 cm^{-1}) are observed in the hydroxyl stretching region. A new band at 3735 cm^{-1} , assigned to octahedral Al-OH groups, is also observed at temperatures below 400°C . This hydroxyl group has been previously reported in AIPON solids.^{26,41}

As for GaN , Ga-OH groups responsible for the band at 3700 cm^{-1} disappear with heating at 300°C , indicating their low thermal stability. The intensity of the 3667 cm^{-1} band increases with temperature, this must be related to two factors: first, the appearance of new Ga-OH groups with such a $\nu(\text{OH})$ vibration (see above) and, second, the increase of the P-OH concentration resulting from the hydrolysis of P-NH_2 with water coming from hydroxyls (Al-OH , Ga-OH) condensation, following eqs 1. Octahedral Al-OH at 3735 cm^{-1} and Ga-OH groups responsible for the band at 3700 cm^{-1} disappear at high temperatures.

Table 3 summarizes the positions and assignments of the IR bands observed in the AlGaPON spectra. For comparative purpose, those of the AIPON and GaN are also included.

DRIFTS Study of the AlGaPO Thermal Treatment Under NH_3 . To study the steps and mechanism of nitridation of AlGaPO , as well as to identify the nitrogenous species involved, the AlGaPON synthesis reaction was repeated inside the DRIFTS cell. Gaseous NH_3 was flowed through the AlGaPO sample, and the temperature increased from room temperature to 650°C , collecting a DRIFTS spectrum after 30 min of stabilization at 100 , 200 , 300 , 400 , 500 , 550 , and 600°C . Results are presented in Figure 5. At room temperature, NH_3 is adsorbed on the Brønsted acid sites of the surface as ammonium ions (1445 cm^{-1} , $\delta_{\text{as}}(\text{HNN})$; 1695 cm^{-1} , $\delta_{\text{a}}(\text{HNN})$; 2700 , 3060 cm^{-1} , $\nu(\text{NH})$). The adsorption of ammonia on Lewis acid sites is also evidenced, although it is not clearly observed since adsorbed

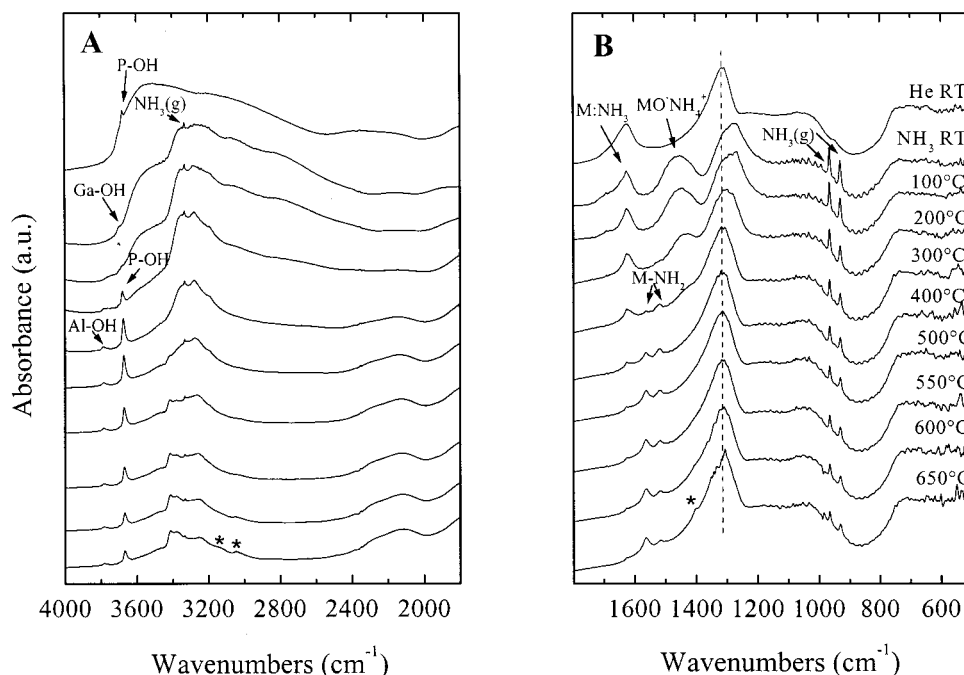


Figure 5. DRIFTS spectra of the AlGaPO sample obtained in situ during the thermal treatment under gaseous NH_3 at the temperatures indicated. Spectra are displayed in two regions: (A) 4000–1800 cm^{-1} ; (B) 1800–600 cm^{-1} (* bands due to NH_4^+ ions adsorbed onto the ZnSe windows of the DRIFTS cell (see ref 29)).

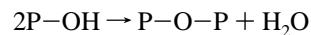
water presents a $\delta_a(\text{HOH})$ bending vibration at about 1624 cm^{-1} which overlaps the bending mode of metal-coordinated NH_3 .

In the framework vibrational region, the adsorption of ammonia produces a shift of the main band to lower wavenumbers due to $\text{P}=\text{O}$ and PO_2 stretching vibrations, from 1310 to 1277 cm^{-1} . This shift is due to the presence of $\text{M}-\text{O}-\text{NH}_4^+$ species ($\text{M} = \text{Al, Ga, P}$), probably decreasing the strength of the $\text{P}=\text{O}$ bonds by H-bond formation.

When the temperature is increased, ammonia adsorption on Brønsted acid sites decreases and disappears at about 400 °C. According to the explanation given above, the elimination of ammonium ions induces the return of the $\text{P}=\text{O}$ band at 1310 cm^{-1} , its original position. Except for this behavior, no change in the lattice vibrations of the AlGaPO solid is observed whatever the temperature. This indicates that, up to this temperature, the bulk structure of the AlGaPO has not been affected, and no oxygen has been replaced by nitrogen atoms. Thus, no real nitridation of the solid has occurred. However, we observe an evolution of the nitrogenous species present on the surface, with the temperature. Besides the observed desorption of NH_4^+ species (from 100 to 400 °C), a band at 1515 cm^{-1} appears at 200 °C. This band is due to $\text{M}-\text{NH}_2$ groups bridged-bonded to the surface of the solid. The intensity of this band increases with temperature up to 300 °C, temperature at which a new band at 1560 cm^{-1} ascribed to free $\text{M}-\text{NH}_2$ species is developed. At 650 °C, bands at 1625, 1560, and 1515 cm^{-1} remain in the spectra showing that coordinated $\text{M}-\text{NH}_3$ and $\text{M}-\text{NH}_2$ species are stable at such high surface temperature.

Another interesting observation is the evolution of the bands in the 4000–2500 cm^{-1} region. At room temperature, just before admitting NH_3 in the DRIFTS cell, the spectrum of the AlGaPO is characterized by the broad absorption of adsorbed water and bands at 3679 and 3510 cm^{-1} due to tetrahedral $\text{P}-\text{OH}$ groups and H-bonded hydroxyl groups, respectively. After introduction of NH_3 , a band at 3700 cm^{-1} due to $\text{Ga}-\text{OH}$ groups becomes visible and the 3679 cm^{-1} band disappears, suggesting that $\text{P}-\text{OH}$ groups are the main Brønsted acid sites responsible for the ammonium adsorption. In agreement with this, when the

temperature is raised, NH_4^+ ions desorption occurs, and this band is restored. In a recent paper, Janin et al.,³⁹ based an IR study of NH_3 and pyridine probe molecule adsorptions, suggest that, since $\text{P}-\text{OH}$ groups have a higher acidity than $\text{Ga}-\text{OH}$ ones in GaPO_4 solids, they are responsible for the weak Brønsted acidity observed in these solids. On the other hand, simultaneously with the ammonium, water is also desorbed, causing the appearance of hydroxyl groups coordinated to tetrahedral aluminum band at 3785 cm^{-1} . The NH stretching vibrations characteristic of coordinated NH_3 are also observed (3414, 3379, and 3259 cm^{-1}). $\text{Ga}-\text{OH}$ groups at 3700 cm^{-1} disappear at very low temperatures (<200 °C), and the intensity of the band at 3670 cm^{-1} passes through a maximum at 400 °C, pointing to a partial development of the condensation reaction



At temperatures above 600 °C, three new bands at 3148, 3046, and 2817 cm^{-1} are developed. As recently shown, they are due to NH_4^+ ions not adsorbed onto the solid surface but on the SeZn windows of the DRIFTS chamber.²⁸

No evidence of a band at about 3330 cm^{-1} , which can be attributed to structural $-\text{NH}-$ species, is detected. This evidences that no bulk nitridation of the oxide is obtained, in good agreement with the analysis of the framework region. The lower NH_3 flow and concentration used in the DRIFTS experiment as compared with those used for the AlGaPON preparation (see Experimental Section) as well as the short nitridation time can explain this phenomenon. However, the evolution of the surface nitrogenous species with temperature can be representative of the first stages of the nitridation process, since nitridation has been described to begin with surface reactions.⁵⁶

The results presented show that, first of all $\text{NH}_3(\text{g})$ is adsorbed onto Lewis acid sites (Al, Ga, or P atoms) and Brønsted acid sites (hydroxyl groups, mainly $\text{P}-\text{OH}$) of the solid. Then, H-bonded $\text{M}-\text{NH}_2$ groups and, later, free $\text{M}-\text{NH}_2$ ones appear. This sequence of formation of surface NH species agrees with

the mechanism for nitrogen incorporation proposed by Mulfinger⁵⁷ and others.^{56,58,59}

Although NH₂ groups can be produced from coordinatively adsorbed NH₃ species or from NH₄⁺ ions, two facts lead us to propose that NH₂ groups initially come from adsorbed NH₄⁺ species: (i) the fact that the H-bonded M–NH₂ groups appear before the free M–NH₂ ones and (ii) the disappearance of ammonium ions simultaneous with the appearance of NH₂ groups. If it is so, as we have proved that ammonium ions are mainly adsorbed on P–OH groups, we must conclude that NH₂ groups are attached essentially to phosphorus atoms. At high temperatures, coordinated ammonia can also react with surface OH groups to form more NH₂ groups.

If the nitridation process were to be continued, –NH– groups would be the next nitrogenous species to be formed. In this sense, a recent ab initio molecular orbital study shows that, from a thermodynamic standpoint, the formation of a terminal NH₂ group in Al–O–P linkages is more favorable than the substitution of a bridging oxygen by a –NH– group.⁶⁰

At last, bulk nitridation will occur. In that sense, it has been proposed that bulk nitridation of AlPO solids occurs once M–NH₂ and –NH– saturation coverage is reached.^{30,31}

Conclusions

The vibrational structure of AlGaPON was studied by comparing the DRIFTS spectra of AlPO, AlGaPO, GaPO, AlPON, and GaN solids. The presence of gallium, with a higher radius than aluminum or phosphorus, produces a shift of the framework bands to lower wavenumbers. The substitution of oxygen atoms by nitrogen (with lower electronegativity) in the network of the AlGaPO solid leads to the collapse of the structure as shown by the broadening and lower definition of the structural bands.

In all nitrated samples (AlPON, AlGaPON and GaN), the same surface nitrogenous species (NH₄⁺, NH₃, –NH₂, and –NH–) with similar vibration bands have been detected, making the identification of the metal atom to which they are attached very difficult.

In the hydroxyl stretching region, we clarified the assignment of the $\nu(\text{OH})$ band at 3700 and 3660 cm^{–1} to Ga–OH and both Ga–OH and tetrahedral P–OH groups.

At last, the study of the thermal treatment under NH₃ of the AlGaPO sample leads us to propose that nitridation begins at the surface of the solid, following the sequence M–O[–]NH₄⁺ and/or M–NH₃ → M–NH₂ → M–NH–M → N^{3–}.

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