XAS structural and electronic investigation of a new type of catalyst: AlGaPON

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Substitution of oxygen by nitrogen in galloaluminophosphate oxides leads to compounds, with properties and applications improved as compared to the oxide. The structural and electronic changes induced by the anionic substitution of oxygen by nitrogen on those amorphous compounds have been studied by XAS. The investigation of the EXAFS and XANES data have allowed us to highlight some structural changes; in particular the existence of mixed tetrahedra XO_xN_y (x being P, Al or Ga) have been demonstrated. Such a study is helpful in understanding the variations in the surface acido-basic properties of these compounds.

Keywords: XAS, electronic structure, AlGaPON, catalyst.

1. Introduction

Galloaluminophosphate oxynitrides have been shown to be highly efficient catalysts in a wide variety of base-catalysed processes (Peltier et al. 1997). The catalytic properties, which are nitrogen-content adjustable, are obviously closely related to the structure of these materials. In this respect XAS which is a useful tool for the investigation of the atomic arrangement and the electronic properties, has been carried out on a series of samples with various nitrogen contents. The samples are prepared by nitridation under ammonia stream of reactive phosphate precursors. X-ray absorption measurements have been recorded at the aluminium, gallium and phosphorus K-edges. The spectra enabled us to characterise the modifications of the local surroundings of these atoms induced by nitridation.

2. Experimental

The XAS experiments have been performed at SuperACO and DCI: Al and P spectra have been recorded on the SA32 soft X-ray beam line using the two crystal monochromator equipped with quartz (10-10) for Al- K edge and Ge (111) for P-K edge, while Ga spectra have been measured on Exafs 13 station using the two crystal monochromator equipped with Si(311). The experimental resolution was of the order of 0.5 eV for Al K, 0.7 eV for P K and 2.5 eV for Ga K. The spectra were calibrated using metallic foils and measured either by Total Electron Yield or by transmission.

3. XANES results

3.1 Crystalline $Al_{0.5}Ga_{0.5}PO_4$

In this paper crystalline $Al_{0.5}Ga_{0.5}PO_4$ has been taken as a reference for the investigation of the structure of the $Al_{0.5}Ga_{0.5}PO_xN_y$ system. As already reported (Guegen et al.

1997), $Al_{0.5}Ga_{0.5}PO_4$ can be considered as consisting of a three-dimensional repetition of slightly deformed AlO_4, GaO_4 and PO_4 tetrahedra. Its structure can thus be compared with that of berlinite, $AlPO_4$, which is isoelectronic to SiO_2, and which can be built up from quartz by alternately replacing the silicon atoms by phosphorous and aluminium atoms, with some corrections to the bond lengths (Schwarsenbach et al. 1966). Because no DOS calculation exists for the studied samples, but since $Al_{0.5}Ga_{0.5}PO_4$ and Quartz (SiO_2) are structurally similar, the electronic band structure of quartz has been considered for comparison (Jollet et al. 1993, Lagarde et al. 1992).

Figure 1 displays the P, Al and Ga K edges recorded in crystalline $Al_{0.5}Ga_{0.5}PO_4$, compared to the Si K edge from quartz. A rather satisfying correspondence between the different edges is observed. The spectra, consisting of one intense white line (followed by minor fine structures) and one broad resonance, lying at about 16-17 eV beyond the white line, are similar for all four elements. Within the dipole approximation the edges reflect the p local DOS on the cation atom. In SiO_2, the main peak (arbitrary scale at 0 eV in Fig. 1) is attributed to antibonding cation-oxygen states, while the minor features come from $p-t_2$ hybridisation between the second neighbour cation-cation pairs (Jollet et al. 1993). These structures can also be interpreted as resulting of multiple scattering (Briois et al. 1993). The broad peak at 17 eV is assigned to a shape resonance arising from the first two shells around the central cation atom (Lagarde et al. 1992). The existence of a core hole on the absorber atom in the final state has been shown to have a considerable influence on the shape of the density of empty states, particularly on cation local DOS, which has a quasi-atomic character (Jollet et al. 1993). Ga K differs slightly from the others, its white line being more broadened. This can be partially explained by the difference in the experimental energy resolution (2.5 eV for Ga and an average value of 0.6 eV for Al, P and Si) and in the core hole width.

In the following, these preliminary interpretations of the XANES will be used as a base for understanding the electronic properties of the $\{Al_{0.5}Ga_{0.5}PO_xN_y\}$ system.
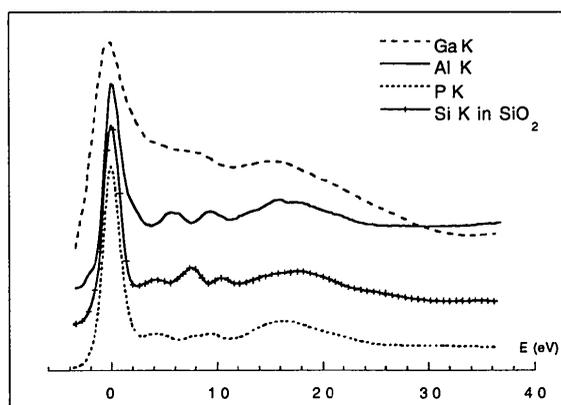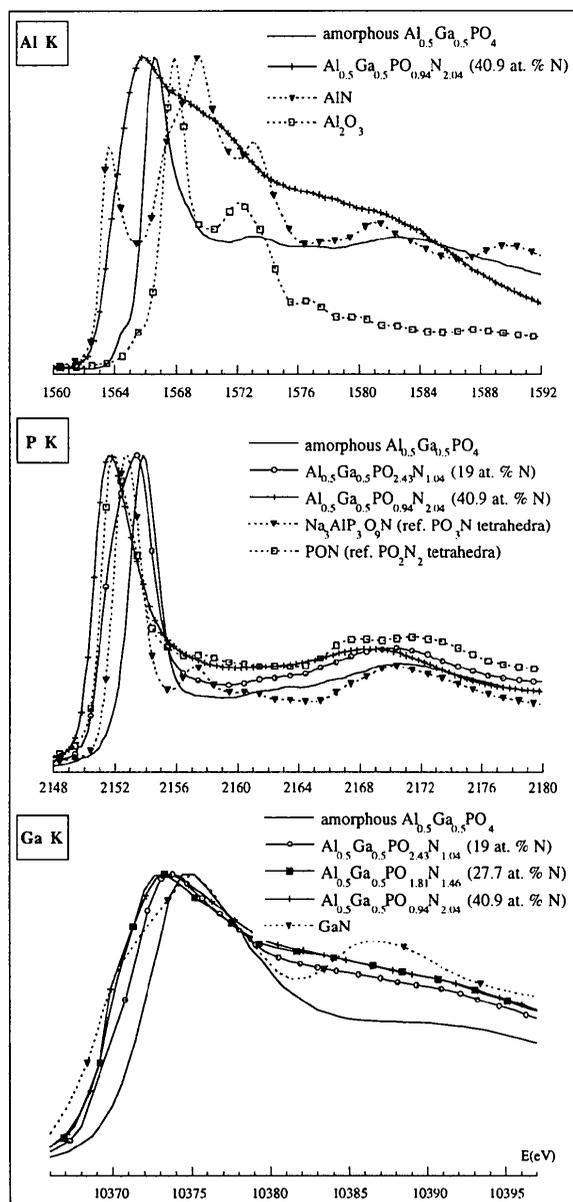

Figure 1
Comparison of Ga, Al and P K edges in crystalline $Al_{0.5}Ga_{0.5}PO_4$ with Si K in SiO_2.
For a clear comparison, the spectra have been normalised, and aligned on the white line.

3.2 Amorphous $Al_{0.5}Ga_{0.5}PO_xN_y$

This paper concerns the study of five $Al_{0.5}Ga_{0.5}PO_xN_y$ compounds corresponding to various nitrogen contents: 0, 9,

19.1, 27.7, 40.9 at. % nitrogen. Figure 2 displays some of the Al, P and Ga XANES spectra compared to those of crystalline references. The XANES in the $Al_{0.5}Ga_{0.5}PO_xN_y$ compounds exhibit similar behaviour: whatever the type of cation, the edges gradually shift towards the lower energy side (the maximum is of about 2 eV) as the nitrogen content increases, while an enlargement of the white line, particularly noticeable in the case of Al K, is simultaneously visible. Both the differences in O and N electronegativities and the fact that the X-N distances are longer than the X-O ones (X being Al, Ga or P), may play a role in the evolution of the XANES (Schwarsenbach et al. 1966).

Figure 2

Al, P and Ga K XANES in the different amorphous $\{Al_{0.5}Ga_{0.5}PON\}$. They are compared to crystalline references: αAl_2O_3 and AlN for aluminium, $Na_3AlP_3O_9N$ (reference of mixed PO_3N tetrahedra) and PON (reference of mixed PO_2N_2 tetrahedra) for phosphorous. The spectra were normalised to the maximum of the edge.

The Al XANES for the $Al_{0.5}Ga_{0.5}PO_xN_y$ with the higher N content have features that roughly mimic the Al XANES for AlN (which corresponds to tetrahedral Al). On the contrary the comparison with the reference of octahedral Al, such as αAl_2O_3, discorders such an environment for Al. This is in agreement with other studies (Ildefonse et al. 1998, Brydson et al. 1992) relating the XANES to the coordination. In particular, it has been shown for Al XANES that two peaks always exist in non-crystalline solids for the octahedral environment, while only one is observed for the tetrahedral one (Ildefonse et al. 1998). The same conclusion can be extended to Ga in $Al_{0.5}Ga_{0.5}PO_xN_y$ when XANES spectra are compared to that of wurtzite-like GaN. The existence of nanophases of those references has thus to be considered in the $Al_{0.5}Ga_{0.5}PO_xN_y$ corresponding to higher nitrogen contents.

On the other hand, the comparison of P K in $Al_{0.5}Ga_{0.5}PO_xN_y$ and in references clearly suggests the presence of mixed tetrahedra around P, when O atoms are substituted for N.

From XANES it can thus be concluded that substitution partially affects the Al, P, and Ga cations environment, which is in agreement with the hybrid features of the corresponding XANES.
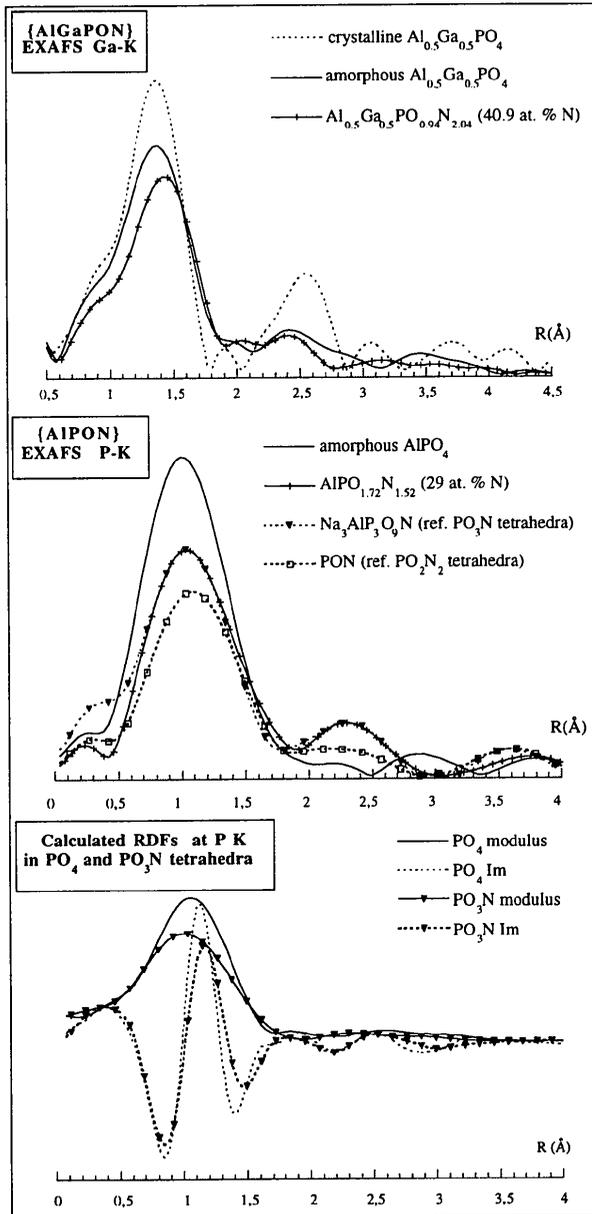
4. EXAFS results

Ga K and P K EXAFS spectra have been collected for the same series of $Al_{0.5}Ga_{0.5}PO_xN_y$, while other similar systems such as $\{AlPON\}$ or $\{GaPON\}$ have also been investigated for comparison. The EXAFS oscillations have been extracted using a fourth-order polynomial to model the atomic absorption beyond the edge with a Lengeler normalisation. We used a k^2 weighting and a Kaiser window with a damping factor of 1.5. For the sake of brevity, we present here only the moduli of the Fourier transform of three samples - 0, 29 and 40.9 at. % nitrogen- (figure 3).

The Fourier transform spectra clearly indicate that only one coordination shell is visible, in agreement with the amorphous structure of the studied compounds. Both in Ga and P environment, the nitrogen content affects mainly the amplitudes of the major peak of the RDF, which corresponds to the first atomic distances Ga-O and Ga-N, and P-O and P-N. A slight shift towards high distances is also visible. The close fit between RDFs for the higher nitrogen content and for the $Na_3AlP_3O_9N$, composed of mixed PO_3N tetrahedra, clearly demonstrates that such an environment exists around P atoms in AlPON systems. In addition preliminary calculations (figure 3), using Feff code (Rehr et al. 1992), which have been performed for PO_4 and PO_3N clusters (with substitutional position of nitrogen), confirm the decrease of the amplitude of the first peak when the N content is increased.

These data confirm the analysis of the XANES, demonstrating that mixed PO_3N tetrahedra are formed around phosphorous atoms. Noticeable changes also occur around the Ga and Al atoms, but a tetrahedral environment seems to be preserved. This first approach will be completed by EXELFS treatment on Al, O and N K edges and by more extended theoretical calculations which are now in progress to quantify these conclusions. In addition, other techniques such as solid state MAS NMR techniques, which are widely used for determining the coordination symmetries of Al and P (Ildefonse et al. 1994, Massiot et al. 1996) will also be investigated to confirm the XAS evidence.

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Figure 3
Moduli of the Fourier transform at the Ga and P edges for $Al_{0.5}Ga_{0.5}PO_xN_y$ and $AlPO_xN_y$ containing different amounts of nitrogen. In the bottom part of the figure are shown the calculated radial distribution functions corresponding to PO_4 and PO_3N tetrahedra.