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# NMR Characterization of the $Na_3AlP_3O_9N$ and $Na_2Mg_2P_3O_9N$ Nitridophosphates: Location of the (NaAl)/$Mg_2$ Substitution

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We report a solid state nuclear magnetic resonance study of $^{23}$Na, $^{27}$Al, and $^{31}$P in two crystalline nitridophosphate phases, $Na_3AlP_3O_9N$ and $Na_2Mg_2P_3O_9N$, including two-dimensional multiple-quantum magic angle spinning (MQ−MAS) experiments on $^{23}$Na to separate overlapping lines. The previously described single-crystal structure of $Na_3AlP_3O_9N$ gives crystallographic examples of $Al(OP)_6$ and $P(O[Al,Na])_2(ONa)(N[P,Na])$ environments and three different environments of sodium: two $Na(O)_6$ and one $Na(O)_6(N)$. From these observations we characterize the modification of the local environment of phosphorus and show that Mg only substitutes Na in the Na2 site of the $Na_2Mg_2P_3O_9N$ structure.

## Introduction

Solid state high-resolution NMR is one of the most powerful tools for the characterization of the local order in crystalline powders and further in amorphous or glassy materials. We report the MAS NMR study of $^{23}$Na, $^{31}$P, and $^{27}$Al in two recently synthesized nitridophosphates: $Na_3AlP_3O_9N$ and $Na_2Mg_2P_3O_9N$. The crystal structure of the $Na_3AlP_3O_9N$ compound was recently determined by X-ray diffraction on a single crystal.[1] The $Na_2Mg_2P_3O_9N$ compound, which has an analogous stoichiometry resulting from the substitution of two Mg atoms for the (Al,Na) couple, was previously only characterized as a powder, and it was thus an open question to locate the sodium sites substituted by magnesium in the (NaAl)/$Mg_2$ substitution.

## Experimental Section

The compounds $Na_3AlP_3O_9N$ and $Na_2Mg_2P_3O_9N$ are the first members of two series of crystalline nitridophosphates having the general formulas $M^I_3M^{III}P_3O_9N$ ($M^I$ = Na, K; $M^{III}$ = Al, Ga, In, Ti, V, Cr, Mn, Fe) and $M^I_2\ M^{II}_2P_3O_9N$ ($M^I$ = Na; $M^{II}$ = Mg, Mn, Fe, Co). Depending on the nitrogen source, the preparation methods involve gas−solid or solid−solid reactions in the 600−800 °C temperature range.[2,3]

$Na_3AlP_3O_9N$ can be obtained from PON phosphorus oxynitride according to

$$Na_2CO_3 + 4NaPO_3 + Al_2O_3 + 2PON \rightarrow 2Na_3AlP_3O_9N + CO_2\uparrow$$

Stoichiometric amounts of sodium carbonate, sodium phosphate, and alumina were first heated at 800 °C in a muffle furnace. In a second step, amorphous PON was finely ground with the decarbonated mixture which was then heated at 800 °C under inert atmosphere.

**Table 1.** $^{31}$P, $^{27}$Al, and 23Na NMR Parameters Obtained for the Different Sites of $Na_3AlP_3O_9N$ and $Na_2Mg_2P_3O_9N$[a]

| | $Na_3AlP_3O_9N$ | | | $Na_2Mg_2P_3O_9N$ | | |
|---|---|---|---|---|---|---|
| site | $\delta_{iso}$ (ppm) | $\Delta_{CS}$ (ppm) | $\eta_{CS}$ | $\delta_{iso}$ (ppm) | $\Delta_{CS}$ (ppm) | $\eta_{CS}$ |
| P | −5 | −80 | 0.95 | 4 | 80 | 0.40 |

| | $Na_3AlP_3O_9N$ | | | | $Na_2Mg_2P_3O^9N$ | | | |
|---|---|---|---|---|---|---|---|---|
| site | $\delta_{iso}$ (ppm) | $C_Q$ (MHz) | $\eta_Q$ | $\delta_{F_1}$ (ppm) | $\delta_{iso}$ (ppm) | $C_Q$ (MHz) | $\eta_Q$ | $\delta_{F_1}$ (ppm) |
| Al | −9 | 0.30 ± 0.05 | 0.0 | | | | | |
| Na1 | 9 | 1.86 | 0.0 | 36 | 9 | 2.20 | 0.0 | 43 |
| Na2 | −9 | 0.84 | 0.0 | −18 | | | | |
| Na3 | −15 | 1.72 | 0.0 | −19 | −15 | 1.40 | 0.0 | −22 |

[a] Positions are given in ppm (±0.5 ppm), $\Delta_{CS}$ (±5 ppm) and $\eta_{CS}$ (±0.05) are the axiality and the asymmetry of the shielding tensor (for $^{31}$P), $C_Q$ (±0.02 MHz) and $\eta_Q$ (±0.05) are the quadrupolar frequency and the quadrupolar asymmetry of the electric field gradient tensor (for $^{23}$Na and $^{27}$Al).

$Na_2Mg_2P_3O_9N$ was preferentially prepared at 700 °C in one step according to the following reaction:

$$2NaPO_3 + 2MgO + 2PON \xrightarrow{\text{inert atm}} Na_2Mg_2P_3O_9N$$

High-resolution MAS (magic angle spinning) NMR spectra of $^{27}$Al, $^{23}$Na, and $^{31}$P were recorded at different spinning rates and under static conditions with a principal field of 7 T on a Bruker MSL 300 spectrometer. The isotropic NMR chemical shift ($\delta_{iso}$) was characterized for each site. For $^{31}$P we report the chemical shift anisotropy tensor parameters characterized by its axiality $\Delta_{CS} = \delta_{33} - \delta_{iso}$ with $|\delta_{33} - \delta_{iso}| \geq |\delta_{11} - \delta_{iso}| \geq |\delta_{22} - \delta_{iso}|$ and its anisotropy $\eta_{CS} = |\delta_{22} - \delta_{11}|/|\delta_{33} - \delta_{iso}|$. For the quadrupolar nuclei ($^{23}$Na and $^{27}$Al) we report the chemical shift $\delta_{iso}$ and the electric field gradient *l* at the nucleus position characterized by the quadrupolar coupling $C_Q = e^2qQ/h = eQV_{zz}/h$ and its anisotropy $\eta_Q = |V_{xx} - V_{yy}|/V_{zz}$.[4] These NMR parameters have been measured for each site by fitting the different experimental spectra with the Bruker Winfit program running on a PC-486 computer.[5] All the measured parameters are reported in Table 1. The chemical shift

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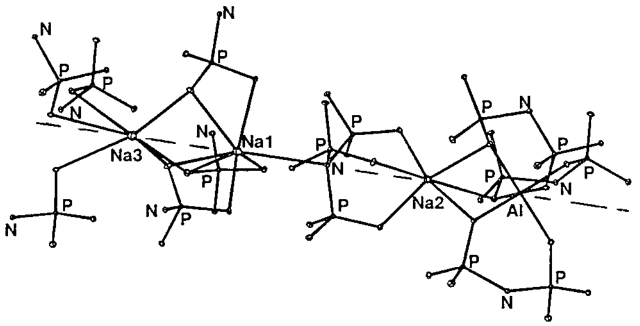

**Figure 1.** Arrangement of the different polyhedra along the [111] direction in the $Na_3AlP_3O_9N$ structure. Reprinted with permision from ref 1. Copyright 1994 Centrale des Revues.

positions are referenced to 1 M $Al(NO_3)_3$ in nitric acid solution for $^{27}Al$, 1 M NaCl in water for $^{23}Na$, and concentrated 85% $H_3PO_4$ for $^{31}P$. To obtain the best resolution of the overlapping lines observed in the $^{23}Na$ spectra and to have an unambiguous interpretation, we used the newly described two-dimensional technique of MQ−MAS (multiple-quantum magic angle spinning)[6−8] that provides an isotropic separation of the resonances of each different sodium site for both studied compounds in a two-dimensional experiment.

## Crystal Structure

The crystal structure of $Na_3AlP_3O_9N$[1] [cubic unit cell, $a$ = 9.274 Å, space group $P2_13$] shows a single hexacoordinated aluminum site $Al(OP)_6$ surrounded by the six equivalent phosphorus atoms. The phosphorus site is tetracoordinated, and each P atom is linked by three oxygen bridges to Al and/or Na and by one nitrogen bridge to two neighboring phosphorus atoms (plus one Na atom): $P(O[Al,Na])_2(ONa)(N[P,Na])$. The sodium nuclei occupy three nonequivalent sites; two of them are hexacoordinated $Na(O)_6$ while the third is a 6+1 coordinated site $Na(O)_6(NP)$. It is of interest to notice that the unique Al site, the unique N site and the three Na sites are located on a $C_3$ axis and thus have an axial local symmetry (Figure 1). $Na_2Mg_2P_3O_9N$ is also cubic—a = 9.252 Å—and its X-ray powder pattern is isotypic with that of $Na_3AlP_3O_9N$.[3]

## Results and Discussion

The $^{27}Al$ MAS NMR spectrum of $Na_3AlP_3O_9N$ presented in Figure 2 was obtained while the rotor was spun at 3 kHz. It is characteristic of a single contribution at $\delta_{iso} = -9$ ppm. This isotropic position is in the upper range of the $Al(OP)_6$ environment described in the literature.[9] The symmetric set of spinning sidebands arise from the first-order quadrupolar splitting of the external (satellite) transitions.[4] With the assumption of a perfectly defined electric field gradient, we measure quadrupolar interaction parameters of $C_Q = 0.3$ MHz and $\eta_Q = 0.2$. The measured asymmetry parameter of 0.2 is not in agreement with the location of the Al site on the $C_3$ axis of the structure. As the static line shape of the Al spectrum (not shown) does not show perfectly defined discontinuities, we can discuss the previous assumption of a perfectly defined electric field gradient. A small (ca. ± 0.05 MHz) Gaussian distribution of $C_Q$ with $\eta_Q = 0.0$ would in fact give a similar set of spinning sideband intensities. As there is currently no simple way of discriminating these two possibilities, we favor the latest one ($C_Q = 0.3 \pm$ MHz, $\eta_Q = 0.0$) according to the single-crystal structure.

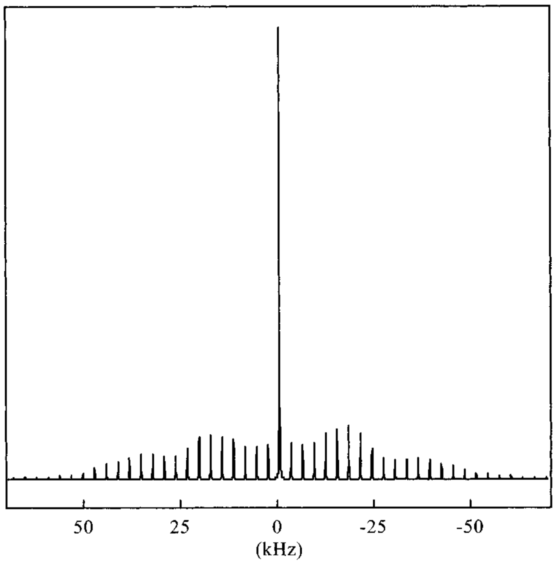

**Figure 2.** $^{27}Al$ MAS NMR spectrum of $Na_3AlP_3O_9N$ obtained with the rotor spinning at 3 kHz. The electric field gradient tensor (quadrupolar interaction) is measured from the intensities of the spinning sidebands of the external (satellite) transitions ($I = {}^5/_2$).

The $^{31}P$ spectra of both $Na_3AlP_3O_9N$ and $Na_2Mg_2P_3O_9N$ are presented in Figure 3 together with their modeling according to the parameters listed in Table 1. Both compounds exhibit a single phosphorus signal consistent with the single atomic position in the structure. The isotropic chemical shift positions are measured at −5 ppm for $Na_3AlP_3O_9N$ and 4 ppm for $Na_2Mg_2P_3O_9N$ in the high-speed MAS spectra (10 kHz spinning rate). Previous work proposed an assignment of $PO_2N_2$ and $PO_3N$ groups to 0, −10 ppm lines, respectively, in sodium phosphate polymerized oxynitride glasses.[10−12] The values are slightly higher in our case for the $PO_3N$ group. At lower spinning rates the static spectrum is modulated into a set of spinning sidebands which can be first interpreted in terms of chemical shift anisotropy at the phosphorus site. While the axialities of the tensors are similar for the two compounds ($|\Delta_{CSA}| = 80$ ppm), the two systems differ for the asymmetry parameters: $\eta_{CSA} = 0.40$ at the phosphorus site of $Na_2Mg_2P_3O_9N$ instead of $\eta_{CSA} = 0.95$ for $Na_3AlP_3O_9N$. The phosphorus NMR parameters are thus sensitive to the replacement of (1 Al + 1 Na) in $Na_3AlP_3O_9N$ by 2 Mg in $Na_2Mg_2P_3O_9N$, both for the isotropic part of the chemical shift tensor ($\delta_{iso}$) and for its anisotropy. This suggests a modification of the local phosphorus environment (bond lengths and bond angles).

Going further in the analysis of the spectra, it is of importance to notice that the line widths, as well as the shapes of the lines in the MAS spectra, vary with the spinning rate and that those parameters do not perfectly render the observed static spectra. Even at the highest spinning rate (15 kHz), the shape of the MAS line consists of a central line with two symmetric shoulders (inset in Figure 3). Previous works on an isolated pair of phosphorus nuclei have shown that it is possible to obtain spinning rate dependent line shapes due to dipolar and $J_2$ couplings between neighboring $^{31}P$.[13−17] In the crystal structure

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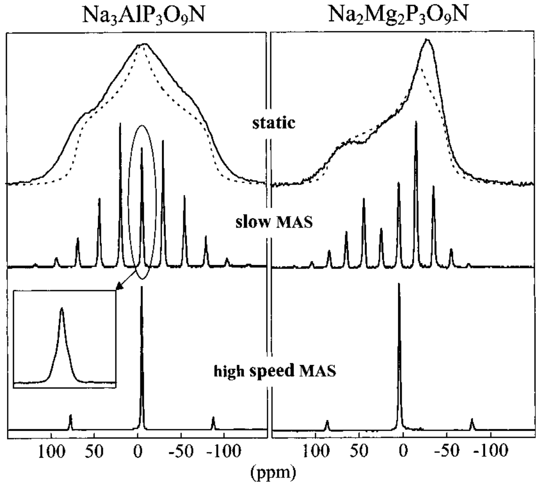

**Figure 3.** $^{31}P$ NMR spectra of $Na_3AlP_3O_9N$ and $Na_2Mg_2P_3O_9N$ under high-speed and MAS, low-speed (3 and 2.4 kHz) MAS and static conditions. Chemical shift anisotropy parameters reported in Table 1 are deduced from the analysis of the spinning sideband intensities obtained at intermediate spinning rate. The dotted line gives the model static line shapes obtained from parameters in Table 1. The inset shows the shape of the spinning sidebands with symmetric shoulders.

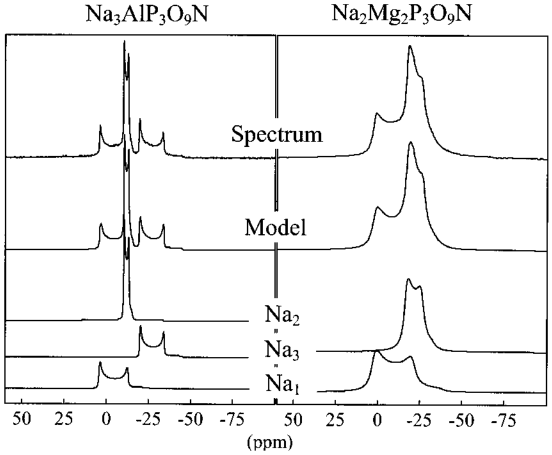

**Figure 4.** $^{23}Na$ NMR spectra of $Na_3AlP_3O_9N$ and $Na_2Mg_2P_3O_9N$ obtained under high-speed (10 kHz) MAS. The spectrum, its model and each individual overlapping component are shown for each compound according to the parameters reported in Table 1.

of $Na_3AlP_3O_9N$, the equivalent phosphorus atoms of $PO_3N$ tetrahedra are grouped by three in $N(PO_3)_3$ groups; each phosphorus is directly linked to one N ($^{14}N$ $I = 1$, $d(N-P) = 1.706$ Å) and indirectly linked to two equivalent phosphorus atoms ($I = {}^1/_2$, $d(P-P) = 2.883$ Å) by a nitrogen bridge. The observed line shapes in the MAS spectra, as well as the fact that the CSA profile does not perfectly model the static spectra (Figure 3), can thus be understood as related to this complex environment.

The $^{23}Na$ spectra of $Na_3AlP_3O_9N$ and $Na_2Mg_2P_3O_9N$ are presented in Figure 4 together with their modeling according to the parameters listed in Table 1. For both compounds, the MAS high-speed spectra (10 kHz) consist of overlapping second-order broadened quadrupolar lines[4] that have to be modeled to retrieve the NMR parameters of each site. Nevertheless, it is now possible to achieve a better separation of each line by running the newly described MQ−MAS (multiple-quantum magic angle spinning) two-dimensional experiment.[6−8] This experiment provides a correlation between the usual MAS (triple quantum filtered) dimension ($F_2$) and an isotropic

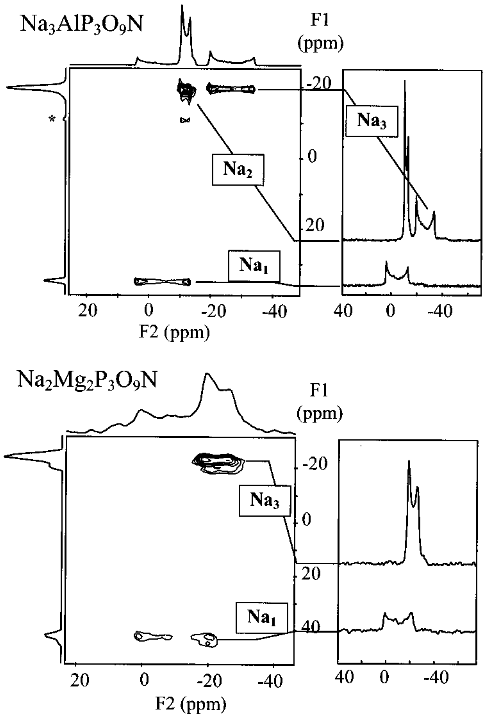

**Figure 5.** $^{23}Na$ NMR MQ−MAS spectra of $Na_3AlP_3O_9N$ and $Na_2Mg_2P_3O_9N$ obtained under high-speed (15 kHz) magic angle spinning. The asterisk (*) marks a spinning sideband. For each compound, we fully separate each component in a two-dimension representation. The vertical axis shows the isotropic spectrum while the horizontal one gives the triple-quantum filtered MAS spectrum of each line.

dimension ($F_1$) in which each site plots as a narrow line. The position in the isotropic dimension ($F_1$) is a function of its NMR parameters ($\delta_{iso}$ is the isotropic chemical shift; $C_Q$ and $\eta_Q$ are the quadrupolar tensor parameters) according to the following equation for a nuclear spin of $I = {}^3/_2$ ($^{23}Na$):[8]

$$\delta_{F_1} = \frac{17}{8}\delta_{iso} + 10^6\frac{C_Q}{4v_0^{\,2}}[1 + \eta_Q^{\,2}/3]$$

The slice taken at the isotropic position is the individual MAS spectrum of each site. The spectra of the two compounds are presented in Figure 5, which shows the obtained two-dimensional contour plots together with the individual cross sections corresponding to the triple-quantum filtered MAS spectrum of each resolved site. The NMR parameters of each site ($\delta_{iso}$, $C_Q$, and $\eta_Q$) have been optimized to obtain the best fit of both the MQ−MAS experiment (position $\delta_{F_1}$ and shape) and high-speed MAS spectra. The MQ−MAS experiment gives the optimal site resolution but is not suited for quantitative analysis due to the $C_Q$ dependence of the multiple-quantum transfer efficiency: the intensities have thus been retrieved from the MAS experiment. These intensities closely match the 1/1/1 ratio of the crystal structure for $Na_3AlP_3O_9N$ and a 1/1 ratio for $Na_2Mg_2P_3O_9N$.

The three $^{23}Na$ lines observed for $Na_3AlP_3O_9N$ have very well defined discontinuities. They correspond to the three non-equivalent sites of the crystal structure, and all have a null quadrupolar interaction asymmetry parameter ($\eta_Q$), in agreement with their location on the $C_3$ axis of the structure. Table 2 presents the first neighbor distances for the three sodium sites. The two Na2 and Na3 sites have a quasi-ideal hourglass shape (trigonal antiprism) with three equivalent oxygen atoms on each side, they both are six coordinated and are expected to have close chemical shift positions. We assign them to the two

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**Table 2.** $Na_x$−$O_y$ Distances (Å) in the $Na_3AlP_3O_9N$ Structure According to Conanec *et al.*[3]

| distances | O1 | O2 | O3 | N |
|---|---|---|---|---|
| Na1 | 2.599 (3×) | 2.514 (3×) |  | 2.8851 |
| Na2 |  | 2.442 (3×) | 2.328 (3×) |  |
| Na3 | 2.825 (3×) |  | 2.377 (3×) |  |

resonances at −9 and −15 ppm. Considering the much greater differences in bond length for the Na3 compared to the Na2 sites and thus the higher distortion of the local environment, the NMR line with the greater quadrupolar interaction (−15 ppm/1.72 MHz) is ascribed to the Na3 site while the second one (−9 ppm/0.84 MHz) is ascribed to the Na2 site. The remaining line (9 ppm/1.86 MHz) is finally ascribed to the Na1 crystalline site. Its higher quadrupolar coupling is consistent with its very distorted geometry implied by the link to the nitrogen site (6 O + 1 N coordination): the $O_1$−$Na_1$−N angle is 81.33°, and thus the three O1 atoms are close to being in equatorial positions with respect to the $C_3$ axis. This higher chemical shift (lower shielding) is consistent with a deshielding effect of the neighboring nitrogen.

In the $^{23}Na$ MAS spectrum (both MAS and MQ−MAS) of $Na_2Mg_2P_3O_9N$, we observe only two lines with axial symmetry ($\eta_Q = 0.0$), still consistent with the $C_3$ structural axis, in the 1/1 ratio. We have to remark that the spectral discontinuities of both sites are less resolved in the MAS spectrum of this second compound; this is usually taken as an indication of less well defined NMR parameters and rendered by a Gaussian distribution of chemical shift and/or quadrupolar coupling $C_Q$ but could also be due to an additional line underneath. Comparing the $^{23}Na$ NMR parameters for the different sites of the two compounds, we note that the observed chemical shifts for $Na_2Mg_2P_3O_9N$ are similar to those ascribed to the positions Na1 and Na3 in $Na_3AlP_3O_9N$. As the MQ−MAS experiment does not show any trace of a component with a chemical shift in area of −9 ppm, we can exclude the presence of a supplemental site of the Na2 type. It thus appears that the substitution of 2 Mg for the (Al + Na) pair occurs on the Al and Na2 positions only. This confirms the previously presented discussion of the $Na_3AlP_3O_9N$ structure compared to the langbeinite $K_2Mg_2(SO_4)_3$ structure, where Mg occupies two structural octahedral positions of Al and Na2 types.[1]

## Conclusion

A $^{31}P$, $^{27}Al$, and $^{23}Na$ high-resolution solid state NMR study of the two newly described $Na_3AlP_3O_9N$ and $Na_2Mg_2P_3O_9N$ crystalline compounds is reported, including a multiple quantum MAS experiment on $^{23}Na$ to fully resolve overlapping lines. We measure and discuss both the isotropic positions ($\delta_{iso}$) and the anisotropy (chemical shift anisotropy for $^{31}P$ and quadrupolar interaction for $^{23}Na$ and $^{27}Al$) of each structural site: $P(O[Al,Na])_2(ONa)(N[P,Na])$, $Al(OP)_6$, $Na(O)_6$, and $Na(O)_6(N)$ and we propose an assignment of the three different $^{23}Na$ sites of the $Na_3AlP_3O_9N$ structure. We finally show that, in the $Na_2Mg_2P_3O_9N$ compound, Mg exlusively substitutes the Al and Na2 sites of the reference structure $Na_3AlP_3O_9N$.

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