

Oxyfluorinated Microporous Compounds. I. Crystal Structure of $(\text{NH}_4)_{0.93}(\text{H}_3\text{O})_{0.07}\text{GaPO}_4(\text{OH})_{0.5}\text{F}_{0.5}$; Reexamination of the Structure of $\text{AlPO}_4\text{-CJ2}$

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The title compounds were prepared from a mixture of 1 M_2O_3 ($M = \text{Ga}$ or Al), 1 P_2O_5 , 2 NH_4F , 1 hexamethylenetetramine, and 80 H_2O by hydrothermal synthesis at 180°C . Their crystal structure was determined by single-crystal X-ray diffraction. They crystallize in space group $P2_12_12_1$, $Z = 8$, with cell parameters $a = 9.593(2) \text{ \AA}$, $b = 9.742(2) \text{ \AA}$, $c = 9.981(2) \text{ \AA}$ and $a = 9.416(8) \text{ \AA}$, $b = 9.563(5) \text{ \AA}$, $c = 9.933(4) \text{ \AA}$ for $M = \text{Ga}$ and Al , respectively. It appears that the aluminophosphate had previously been prepared and called $\text{AlPO}_4\text{-CJ2}$, but was poorly characterized. The crystal structure of these compounds can be described as a three-dimensional network of PO_4 tetrahedra sharing vertices with triangular bipyramids MX_5 and octahedra MX_6 ($X = \text{O}^{2-}, \text{OH}^-$ or F^-). These polyhedra form eight-membered rings and delimit channels in which ammonium groups occupy two types of sites. Depending on M , fluorine atoms occupy one or two different sites, either in full occupancy or in statistical occupancy with hydroxyl groups. Descriptions of the structures are presented, as well as structural comparisons with morinite and minyulite. © 1993 Academic Press, Inc.

Introduction

The discovery by Wilson *et al.* (1) of new three-dimensional aluminophosphates prepared with amines or quaternary ammonium salts as templates, has renewed the activity on microporous compounds; up to now, more than 30 forms of AlPO_4 with a ratio $\text{Al/P} = 1$ (named $\text{AlPO}_4\text{-}n$) with a three-dimensional network have been characterized (see refs. (2, 3), for example). Since 1985 (4), new crystalline materials with open framework structures have been synthesized using gallium instead of aluminum. The latest example of a microporous gallate is cloverite (5), which exhibits the largest pores ever evidenced. In addition, the introduction of fluorine into the framework using the method of Kessler (6) has proved to increase the catalytic properties of these compounds.

Following the same idea, we have synthesized a new three-dimensional gallophosphate whose X-ray powder diffraction pattern shows strong similarities with that of a recently discovered aluminophosphate called $\text{AlPO}_4\text{-CJ2}$ (7). Several structural ambiguities exist in the crystal structure of the latter compound: the authors claim without any support the presence of fluorine in the framework and of oxygen belonging to water molecules in the cavities. Moreover, from their data, it is impossible to assign a correct stoichiometry to the compound, whose formula, without regard to electric neutrality, could be $\text{Al}_2\text{P}_2\text{O}_{11}\text{F}$ or $\text{Al}_2\text{P}_2\text{O}_8(\text{H}_2\text{O})$, 2 H_2O as well. This incited us to reexamine this structure. The results of this study concerning both the aluminophosphate and the gallophosphate and involving single crystal X-ray diffraction, SHG measurements, and chemical and valence bond

analyses are presented here. They allowed us to assign the formula $(\text{NH}_4)_{1-y}(\text{H}_3\text{O})_y \text{MPO}_4(\text{OH})_{0.5-x}\text{F}_{0.5+x}$ (with $x = 0.17$ and $x = 0$, $y = 0.12$ and $y = 0.07$ for $M = \text{Al}$ and Ga , respectively) to these compounds.

Experimental

The syntheses were carried out hydrothermally under the following experimental conditions: reaction mixtures with molecular ratio 1 M_2O_3 ($M = \text{Al}, \text{Ga}$): 1 P_2O_5 : 2 NH_4F : 1 hexamethylenetetramine: 80 H_2O were placed in a stainless steel autoclave lined with Teflon and heated at 180°C for 3 days. The resulting products were filtered off, washed with distilled water, and dried at room temperature. Note that, for the aluminate, the same phase is obtained with cyclohexylamine, piperazine, piperidine, 1,4-diazabicyclo [2.2.2] octane, and N,N,N',N' -tetramethylethylenediamine as templates but not with quaternary ammonium salts like tetramethylammonium hydroxide.

Colorless single crystals were selected from the sample for structural analysis by X-ray diffraction. Their qualities were tested by optical observation and Laue photographs. The noncentric character was confirmed for the aluminophosphate by a positive test in a SHG measurement. Intensity data were collected on a Siemens AED-2 four-circle diffractometer with conditions of measurement reported in Table I. The scattering factors and anomalous dispersion corrections for all atoms are taken from the International Tables for X-Ray Crystallography. The structure was refined with the SHELX-76 (8) program and the two enantiomeric species were tested. The best result is presented here. Weighting factor, secondary extinction, and absorption corrections were applied to the gallium compound. In total, 172 and 173 parameters (including weighting factor) were used during the final refinement for the aluminophosphate and the gallophosphate, respectively. Atomic positions and isotropic thermal parameters

of the hydrogen atoms were refined with constraints on N–H and H–H distances.

The ammonium content was analyzed in different samples, using a classical technique: after reaction with NaOH, NH_3 evolves and is titrated by a 0.1 *N* solution of H_2SO_4 . The fluorine content was determined by the potentiometric method with a fluorine-specific electrode.

Structure Refinement

A preliminary refinement was carried out with a limited number of reflections ($2\theta < 40^\circ$), starting from Yu's positional atomic parameters (7), assuming isotropic thermal factors and gallium replacing aluminum for the gallophosphate. The difference Fourier syntheses located nine main residues with electron density around 1 electron/ \AA^3 :

- two groups of four residues in approximate tetrahedral position around the atoms labeled by Yu as O(10) and O(11) within the channels, suggesting the presence of ammonium ions.

- a residue at about 1 \AA from oxygen O(9) (Yu's label) bridging two metal atoms, suggesting the presence of a hydroxyl group (see below).

Further refinements, including all recorded reflections and the anisotropic motion of all nonhydrogen atoms, were performed assuming nitrogen atoms to be located at the center of the tetrahedron and hydrogen atoms at the residue positions. From the results and the subsequent valence bond analysis (see below), it appeared that:

- the assignment by Yu of the F(1) site as exclusively occupied by fluorine was correct.

- the presence of an oxygen atom alone or a water molecule on O(9) site was very unlikely. The hypothesis of an hydroxyl group seemed more satisfying. An abnormally low thermal motion together with a weak residue close to this site suggested the possibility of a partial substitution of the hydroxyl group by fluorine.

TABLE I
 CONDITIONS OF THE X-RAY DATA COLLECTION OF $(\text{NH}_4)_{0.88}(\text{H}_3\text{O})_{0.12}\text{AlPO}_4(\text{OH})_{0.33}\text{F}_{0.67}$ ($\text{AlPO}_4\text{-CJ2}$) AND
 $(\text{NH}_4)_{0.93}(\text{H}_3\text{O})_{0.07}\text{GaPO}_4(\text{OH})_{0.5}\text{F}_{0.5}$ (IN BRACKETS)

Determination of cell parameters	44 reflections at $2\theta \approx 30^\circ$ [40 reflections]
Space group	$P2_12_1$ (No. 19)
Cell dimensions	$a = 9.416(8) \text{ \AA}$ [$a = 9.593(2) \text{ \AA}$] $b = 9.563(5) \text{ \AA}$ [$b = 9.742(2) \text{ \AA}$] $c = 9.933(4) \text{ \AA}$ [$c = 9.981(2) \text{ \AA}$]
Volume/ Z	$894.5(9) \text{ \AA}^3$ [$932.7(3) \text{ \AA}^3$] $Z = 8$
Wavelength/monochromator	0.71069 \AA (MoK α)/graphite
Temperature	293 K
Scan mode	ω - 2θ
Step scan	$37 \leq N \leq 48$ [$37 \leq N \leq 45$], every 0.035° and 4 sec
Aperture	$3.5 \times 3.5 \text{ mm}^2$
Crystal dimensions	$0.30 \times 0.30 \times 0.40 \text{ mm}^3$ [$0.11 \times 0.15 \times 0.17$]
Absorption corrections	Gaussian method
Transmission factors	$T_{\min} = 0.415$; $T_{\max} = 0.577$ for the gallophosphate
Absorption coefficient	$\mu = 7.2 \text{ cm}^{-1}$ [61.7]
Angular range of data collection	$2\theta \leq 100^\circ$ [$2\theta \leq 80^\circ$]
Range of measured h, k, l	$0 \leq h \leq 20$; $0 \leq k \leq 20$; $0 \leq l \leq 21 - 19 \leq h \leq 0$; $-20 \leq k \leq 0$; $-21 \leq l \leq 0$ $[0 \leq h \leq 17$; $0 \leq k \leq 17$; $0 \leq l \leq 18]$ $[-17 \leq h \leq 0$; $-17 \leq k \leq 0$; $-18 \leq l \leq 0]$ $[-6 \ 0 \ -4$; $0 \ -4 \ 6$; $0 \ 4 \ 6$ [$2 \ 5 \ 0$; $0 \ 3 \ 7$; $6 \ 0 \ 4$]
Standard reflections (3)	
Measured every	60 min
Maximum intensity variation	2.7% [4.4%]
Measured reflections	10,436 [6540]
Independent reflections ($ F > 6\sigma(F)$)	8158 [4951]
Weight	unit [$w = 0.557/(\sigma^2(F) + 0.0002F^2)$]
Secondary extinction	$X = 0.0015$ for the gallophosphate
Number of refined parameters	172 [173]
Final Fourier residuals	-0.86 to $+1.12 e \text{ \AA}^{-3}$ $[-1.72$ to $+3.47 e \text{ \AA}^{-3}$ at about 0.6 \AA from gallium atoms]
R/R_w	$0.024/0.024$ [$0.027/0.028$]

—the coordination tetrahedron of nitrogen N(2) was significantly more distorted than that of nitrogen N(1), especially in the aluminophosphate. Chemical analyses prove the existence of ammonium ions in both compounds, but with ratios NH_4/MPO_4 smaller than 1, 0.88(5) and 0.93(5) per MPO_4 unit for $M = \text{Ga}$ or Al , respectively, suggesting a partial substitution of NH_4^+ by H_3O^+ . The distortion of $\text{N}(2)\text{H}_4^+$ ammonium groups might result from such a substitution. NMR measurements (see part II (9)) confirmed the presence of H_3O^+ in the structure and showed that substitution occurs exclusively on the N(2) site. No attempts to refine the

$\text{N}(2)\text{H}_4^+/\text{H}_3\text{O}^+$ balance from X-ray diffraction were carried out because of the close similarities between the two groups.

For the final refinements, hydrogen atoms of the ammonium groups were fixed equidistant from each other. The reliability factor converged to $R = 0.024$ ($R_w = 0.024$) for the aluminate and $R = 0.027$ ($R_w = 0.028$) for the gallate.

For the aluminophosphate, the occupancy of the partially substituted site refines to $0.35(2) \text{ F}^-$ and $0.65(2) \text{ OH}^-$ on the O(9) site. The chemical analysis, giving $0.63(5) \text{ F}^-$ per AlPO_4 unit, interpreted as one F^- on the F(1) site and 0.26 F^- on the O(9) site, confirms this point. For the gallophosphate,

TABLE II
 ATOMIC COORDINATES AND MEAN-SQUARE DISPLACEMENTS FOR
 $(\text{NH}_4)_{0.88}(\text{H}_3\text{O})_{0.12}\text{AlPO}_4(\text{OH})_{0.33}\text{F}_{0.67}(\text{AlPO}_4\text{-CJ2})$ AND $(\text{NH}_4)_{0.93}(\text{H}_3\text{O})_{0.07}\text{GaPO}_4(\text{OH})_{0.5}\text{F}_{0.5}$
 (IN ITALICS)

Atom	X	Y	Z	B_{eq}
P(1)	0.4231(1) <i>0.4207(1)</i>	0.2081(1) <i>0.2030(1)</i>	0.3581(1) <i>0.3597(1)</i>	0.41(1) <i>0.46(1)</i>
P(2)	0.9184(1) <i>0.9239(1)</i>	0.9853(1) <i>0.9823(1)</i>	0.3619(1) <i>0.3628(1)</i>	0.45(1) <i>0.45(1)</i>
Al(1) Ga(1)	0.6020(1) <i>0.6011(1)</i>	0.2373(1) <i>0.2409(1)</i>	0.6401(1) <i>0.6416(1)</i>	0.43(1) <i>0.45(1)</i>
Al(2) Ga(2)	0.6522(1) <i>0.6531(1)</i>	0.0250(1) <i>0.0194(1)</i>	0.1771(1) <i>0.1779(1)</i>	0.48(1) <i>0.51(1)</i>
O(1)	0.4319(1) <i>0.4311(2)</i>	0.3481(1) <i>0.3374(2)</i>	0.2855(1) <i>0.2822(2)</i>	0.77(2) <i>0.89(5)</i>
O(2)	0.7619(1) <i>0.7687(2)</i>	0.0212(1) <i>0.0168(2)</i>	0.3374(1) <i>0.3417(2)</i>	0.87(2) <i>1.02(5)</i>
O(3)	0.5520(1) <i>0.5422(2)</i>	0.0317(1) <i>0.0281(2)</i>	0.0119(1) <i>0.0121(2)</i>	0.78(2) <i>0.80(4)</i>
O(4)	0.4885(1) <i>0.4709(2)</i>	0.2161(1) <i>0.2194(2)</i>	0.4989(1) <i>0.5044(2)</i>	1.17(3) <i>1.37(6)</i>
O(5)	0.0176(1) <i>0.0177(2)</i>	0.0958(1) <i>0.0886(2)</i>	0.3006(1) <i>0.2934(2)</i>	0.87(3) <i>0.87(5)</i>
O(6)	0.5461(1) <i>0.5431(2)</i>	0.1562(1) <i>0.1599(2)</i>	0.7937(1) <i>0.8005(2)</i>	0.83(2) <i>0.88(5)</i>
O(7)	0.4942(1) <i>0.4979(2)</i>	0.0953(1) <i>0.0888(2)</i>	0.2738(1) <i>0.2870(2)</i>	0.91(3) <i>1.04(5)</i>
O(8)	0.2660(1) <i>0.2670(2)</i>	0.1649(1) <i>0.1561(2)</i>	0.3785(1) <i>0.3720(2)</i>	0.94(3) <i>1.20(6)</i>
O(9)	0.6946(1) <i>0.6918(2)</i>	0.0694(1) <i>0.0721(2)</i>	0.5943(1) <i>0.5881(2)</i>	0.86(5) <i>0.69(4)</i>
N(1)	0.2442(2) <i>0.2419(3)</i>	0.0860(2) <i>0.0901(3)</i>	0.6856(2) <i>0.6873(3)</i>	1.42(4) <i>1.74(8)</i>
N(2)	0.4725(2) <i>0.4745(3)</i>	0.3377(2) <i>0.3393(3)</i>	0.0061(2) <i>0.0047(3)</i>	1.94(6) <i>2.21(4)</i>
F(1)	0.7185(1) <i>0.7167(2)</i>	0.1976(1) <i>0.1995(2)</i>	0.1366(1) <i>0.1365(2)</i>	1.11(3) <i>1.43(5)</i>
H(1)	0.305(3) <i>0.289(4)</i>	0.032(3) <i>0.026(3)</i>	0.716(3) <i>0.715(4)</i>	4.0(4) <i>4.1(5)</i>
H(2)	0.243(4) <i>0.255(5)</i>	0.159(2) <i>0.159(3)</i>	0.730(3) <i>0.736(4)</i>	4.0(4) <i>4.1(5)</i>

TABLE II—Continued

Atom	X	Y	Z	B_{eq}
H(3)	0.263(4)	0.104(3)	0.606(2)	4.0(4)
	0.159(2)	0.072(4)	0.682(5)	4.1(5)
H(4)	0.166(2)	0.046(3)	0.690(3)	4.0(4)
	0.272(5)	0.112(4)	0.610(2)	4.1(5)
H(5)	0.447(4)	0.376(3)	0.066(2)	4.0(4)
	0.534(4)	0.281(4)	0.975(4)	4.1(5)
H(6)	0.526(3)	0.283(3)	0.028(3)	4.0(4)
	0.400(3)	0.330(5)	0.958(4)	4.1(5)
H(7)	0.506(3)	0.385(3)	0.955(3)	4.0(4)
	0.456(4)	0.320(4)	0.085(2)	4.1(5)
H(8)	0.411(3)	0.300(3)	0.973(3)	4.0(4)
	0.504(4)	0.419(2)	0.996(4)	4.1(5)
H(9)	0.706(5)	0.074(5)	0.497(5)	4.0(4)
	0.699(3)	0.060(3)	0.504(3)	4.1(5)

Note. B_{eq} (\AA^2) is defined as: $B_{eq} = 8\pi^2(U_{11} + U_{22} + U_{33})/3$.

the refinement of the occupancy factor of fluorine and the hydroxyl group on the O(9) site pointed out the absence of fluorine on this position, in good agreement with the chemical analysis with 0.50(5) F^- per GaPO_4 unit (interpreted as one F^- on the F(1) site).

The chemical formula of $\text{AlPO}_4\text{-CJ2}$ is thus found to be $(\text{NH}_4)_{0.88}(\text{H}_3\text{O})_{0.12}\text{AlPO}_4(\text{OH})_{0.33}\text{F}_{0.67}$, and that of the gallate is $(\text{NH}_4)_{0.93}(\text{H}_3\text{O})_{0.07}\text{GaPO}_4(\text{OH})_{0.5}\text{F}_{0.5}$. The stoichiometry of these two phosphates differ only in fluorine content, probably in relation to the difference of acidity between Al^{3+} and Ga^{3+} .

The atomic coordinates and anisotropic thermal parameters of all nonhydrogen atoms are reported in Tables II and III, respectively. Selected interatomic distances and bond angles are listed in Table IV. An interesting feature is the fivefold coordination (trigonal bipyramid) of one of the two metal atoms M ($M = \text{Al}, \text{Ga}$).

The N–H distances, around 0.8 \AA , are comparable to those observed by X-ray diffraction in other compounds with ammo-

niun groups. These distances are shorter than the internuclear distances observed by neutron diffraction or NMR techniques (typically 1.03 \AA in NH_4NO_3). As a matter of fact, in this case, the X-ray diffraction technique, which is sensitive to electron clouds, usually gives shorter interatomic distances because the maximum of electron density is shifted from the nucleus of the hydrogen atom toward the nitrogen atom (covalent bonding).

Table V gives the results of the bond valence calculation for the aluminophosphate and gallophosphate.

Description of the Structure and Discussion

The framework of the structure consists of a three-dimensional network of PO_4 tetrahedra, MX_5 ($M = \text{Al}, \text{Ga}$; $X = \text{O}^{2-}, \text{OH}^-, \text{F}^-$) trigonal bipyramids, and MX_6 ($M = \text{Al}, \text{Ga}$; $X = \text{O}^{2-}, \text{OH}^-, \text{F}^-$) octahedra sharing vertices. In the aluminophosphate, the anion shared by aluminum coordination polyhedra is fluorine or oxygen statistically,

TABLE III
ANISOTROPIC THERMAL PARAMETERS^(a) FOR $(\text{NH}_4)_{0.88}(\text{H}_3\text{O})_{0.12}\text{AlPO}_4(\text{OH})_{0.33}\text{F}_{0.67}(\text{AlPO}_4\text{-CJ2})$ AND
 $(\text{NH}_4)_{0.93}(\text{H}_3\text{O})_{0.07}\text{GaPO}_4(\text{OH})_{0.5}\text{F}_{0.5}$ (IN ITALICS) ($U_{ij} \times 10^4$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P(1)	46(1) 49(2)	53(1) 57(2)	55(1) 68(2)	-6(1) -6(1)	-6(1) -5(2)	7(1) 10(1)
P(2)	65(1) 56(2)	56(1) 61(2)	49(1) 55(2)	-6(1) -7(2)	-4(1) -3(1)	-5(1) -4(1)
Al(1) <i>Ga(1)</i>	51(1) 54(1)	60(1) 57(1)	51(1) 60(1)	5(1) 5(1)	-3(1) -1(1)	-1(1) 0(1)
Al(2) <i>Ga(2)</i>	62(1) 59(1)	60(1) 67(1)	61(1) 67(1)	-2(1) -3(1)	1(1) 0(1)	5(1) 9(1)
O(1)	120(3) 168(7)	70(3) 66(5)	103(3) 103(6)	9(2) 12(5)	21(3) 41(5)	7(2) 9(5)
O(2)	81(3) 74(6)	167(4) 225(7)	84(3) 88(6)	-21(3) -33(6)	-11(2) -19(4)	22(3) 26(6)
O(3)	110(3) 103(6)	127(3) 140(6)	61(3) 61(5)	6(2) 18(5)	3(2) 3(4)	14(3) 19(5)
O(4)	176(4) 238(9)	165(4) 177(8)	103(3) 107(6)	-19(3) -38(6)	-73(3) -92(6)	25(3) 69(7)
O(5)	128(3) 138(6)	96(3) 97(6)	105(3) 96(6)	2(2) 6(5)	2(3) 8(5)	-42(3) -43(5)
O(6)	145(4) 165(7)	80(3) 82(5)	89(3) 89(6)	25(2) 25(5)	26(3) 34(5)	20(3) 38(5)
O(7)	110(3) 138(7)	99(3) 93(6)	137(3) 165(7)	-34(3) -28(5)	36(3) 52(6)	24(3) 36(5)
O(8)	64(3) 47(5)	91(3) 94(6)	203(5) 313(10)	19(3) 18(7)	7(3) 7(6)	1(2) 11(5)
O(9)	112(6) 89(5)	104(6) 101(6)	110(6) 73(5)	-4(4) -10(4)	17(5) -4(4)	30(4) 24(5)
N(1)	144(5) 172(9)	185(6) 219(10)	213(6) 267(12)	23(5) 50(9)	20(5) 32(9)	-3(4) -1(8)
N(2)	319(9) 377(15)	280(8) 287(12)	137(5) 160(9)	-15(5) -30(9)	-12(6) 0(10)	128(7) 176(12)
F(1)	149(3) 176(7)	88(3) 102(5)	185(4) 264(8)	10(3) 23(6)	10(3) 12(7)	-28(3) -37(5)

^(a) The vibrational coefficients refer to the expression: $T = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$.

the oxygen being bound to a hydrogen atom to form a hydroxyl group. In the gallophosphate, two gallium coordination polyhedra share a hydroxyl group exclusively.

The basic building unit of the three-dimensional structure (Fig. 1), $M_2P_2O_{12}FX$ ($X = \text{OH}^-$, F^- for $M = \text{Al}$ and $X = \text{OH}^-$ for $M = \text{Ga}$), consists of two PO_4 tetrahedra, sharing corners with one MX_6 octahedron and one MX_5 trigonal bipyramid. In the octa-

hedron, F(1) fluorine is terminal. Topologically, this type of asymmetric unit is related to those found in morinite (12) and minyulite (13), but in these last compounds, aluminum atoms are both sixfold coordinated. A hydroxyl group in morinite and a fluorine group in minyulite bridge the two aluminum atoms.

In the (a,b) plane, the units are linked by corners to form a layer at $z = \frac{1}{4}$ (Fig. 2) and

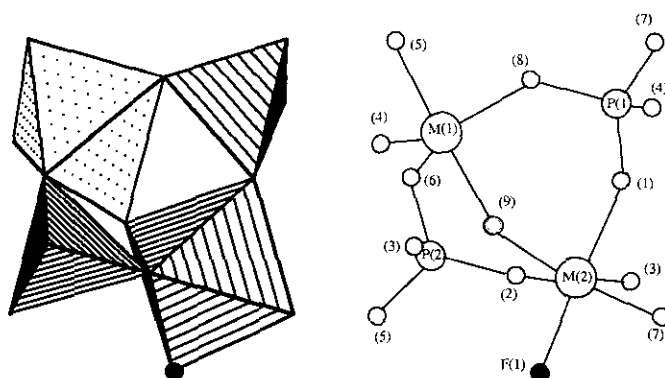


FIG. 1. Basic asymmetric unit $M_2P_2O_{12}FX$ ($M = \text{Al, Ga}$; $X = \text{OH}^-, \text{F}^-$). Labeled small circles display the oxygen atoms; grey circle corresponds to the O(9) site, which is statistically occupied by either a hydroxyl group or a fluorine atom in $(\text{NH}_4)_{0.88}(\text{H}_3\text{O})_{0.12}\text{AlPO}_4(\text{OH})_{0.33}\text{F}_{0.67}$ (AIPO₄-CJ2), and fully occupied by a hydroxyl group in $(\text{NH}_4)_{0.93}(\text{H}_3\text{O})_{0.07}\text{GaPO}_4(\text{OH})_{0.5}\text{F}_{0.5}$.

create corrugated rings with eight cations (metal or phosphorus, alternatively). The upper layer at $z = \frac{3}{4}$ derives from that at $z = \frac{1}{4}$ by a rotation of 180° (2_1 axis) as shown in Figs. 3 and 4. A closely related layered arrangement is reported in minyulite where

the asymmetric units form isolated sheets, while in morinite the asymmetric units form isolated clusters.

The eight-membered rings delimit straight channels along the c axis which contain $\text{N}(1)\text{H}_4^+$ ammonium groups. Puckered chan-

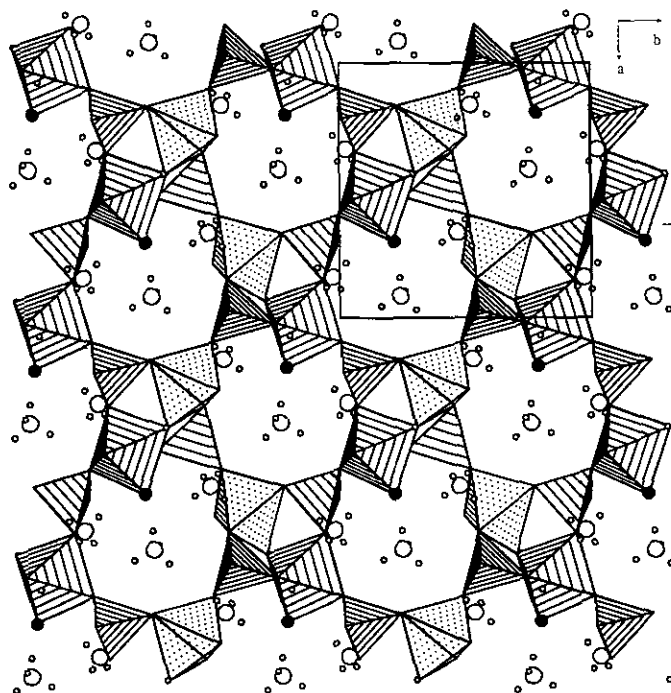


FIG. 2. Projection of the structure onto the 001 plane ($0 < z < \frac{1}{2}$).

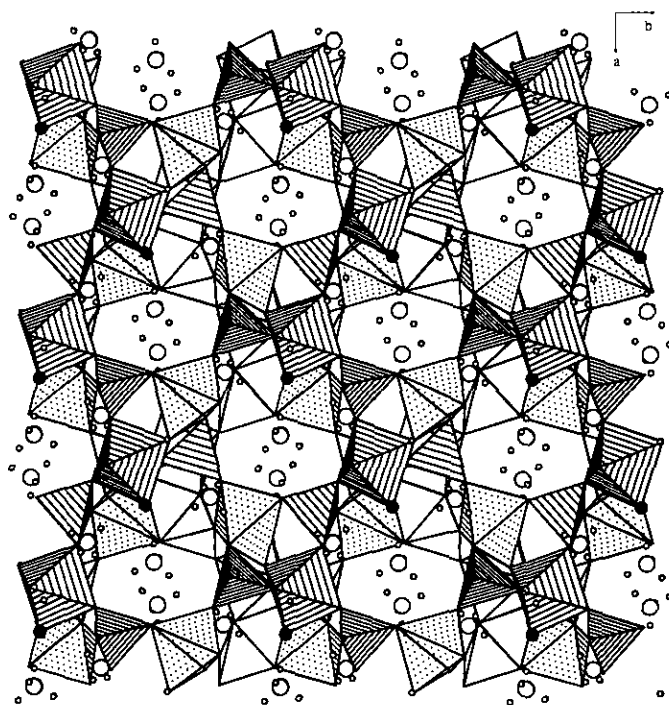


FIG. 3. Projection of the structure onto the 001 plane ($0 < z < 1$) showing the stacking of two layers.

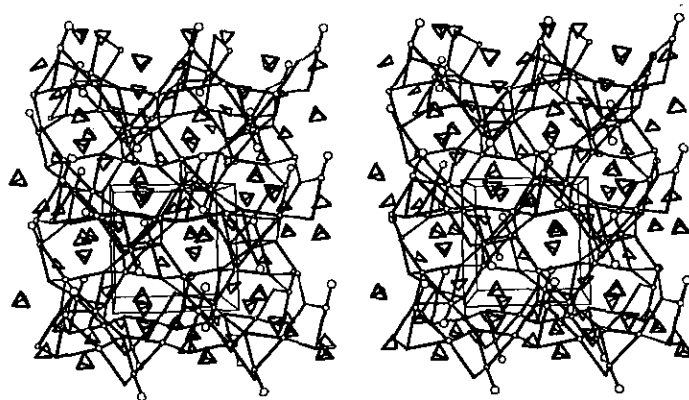


FIG. 4. Stereoview of the $(\text{NH}_4)_{1-y}(\text{H}_3\text{O})_y\text{MPO}_4(\text{OH})_{0.5-x}\text{F}_{0.5+x}$ structure along c . Each line represents a branch connecting two nodes occupied by an aluminum atom (small circle) and a phosphorus atom (unmarked). Fluorine atoms (large circles) are shown as well as ammonium group tetrahedra.

TABLE IV
 INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN
 $(\text{NH}_4)_{0.88}(\text{H}_3\text{O})_{0.12}\text{AlPO}_4(\text{OH})_{0.33}\text{F}_{0.67}(\text{AlPO}_4\text{-CJ2})$ AND
 $(\text{NH}_4)_{0.95}(\text{H}_3\text{O})_{0.07}\text{GaPO}_4(\text{OH})_{0.5}\text{F}_{0.5}$ (IN BRACKETS)

P(1)O ₄ tetrahedron					
P(1)-O(7)	1.521(1)	[1.522(1)]	O(1)-P(1)-O(7)	109.8(1)	[110.8(1)]
P(1)-O(1)	1.523(1)	[1.523(1)]	O(4)-P(1)-O(7)	111.2(1)	[111.9(1)]
P(1)-O(4)	1.530(1)	[1.531(1)]	O(8)-P(1)-O(7)	107.7(1)	[106.5(1)]
P(1)-O(8)	1.549(1)	[1.549(1)]	O(4)-P(1)-O(1)	111.5(1)	[111.7(1)]
			O(8)-P(1)-O(1)	110.4(1)	[110.9(1)]
			O(8)-P(1)-O(4)	106.1(1)	[104.8(1)]
P(2)O ₄ tetrahedron					
P(2)-O(3)	1.525(2)	[1.529(2)]	O(2)-P(2)-O(3)	110.8(1)	[110.7(1)]
P(2)-O(2)	1.533(1)	[1.541(1)]	O(5)-P(2)-O(3)	110.5(1)	[111.1(1)]
P(2)-O(5)	1.536(2)	[1.537(2)]	O(6)-P(2)-O(3)	107.1(1)	[106.7(1)]
P(2)-O(6)	1.550(1)	[1.551(1)]	O(5)-P(2)-O(2)	111.6(1)	[110.9(1)]
			O(6)-P(2)-O(2)	109.5(1)	[109.7(1)]
			O(6)-P(2)-O(5)	107.2(1)	[107.6(1)]
M(1)O ₅ trigonal bipyramid					
M(1)-O(4)	1.775(1)	[1.865(1)]	O(6)-M(1)-O(4)	116.5(1)	[112.3(1)]
M(1)-O(6)	1.791(2)	[1.857(2)]	O(8)-M(1)-O(4)	119.4(1)	[124.9(1)]
M(1)-O(8)	1.815(1)	[1.886(1)]	O(5)-M(1)-O(4)	95.2(1)	[93.7(1)]
M(1)-O(5)	1.878(1)	[1.955(1)]	O(9)-M(1)-O(4)	89.5(1)	[90.2(1)]
M(1)-O(9)	1.883(1)	[1.936(1)]	O(8)-M(1)-O(6)	124.1(1)	[122.7(1)]
			O(5)-M(1)-O(6)	88.7(1)	[87.4(1)]
			O(9)-M(1)-O(6)	88.4(1)	[90.5(1)]
			O(5)-M(1)-O(8)	87.4(1)	[85.2(1)]
			O(9)-M(1)-O(8)	91.2(1)	[93.0(1)]
			O(9)-M(1)-O(5)	175.2(1)	[176.0(1)]
M(2)O ₅ F octahedron					
M(2)-F(1)	1.806(2)	[1.903(2)]	O(9)-M(2)-F(1)	94.6(1)	[94.4(1)]
M(2)-O(9)	1.889(1)	[1.952(1)]	O(3)-M(2)-F(1)	87.6(1)	[87.2(1)]
M(2)-O(3)	1.894(2)	[1.969(2)]	O(7)-M(2)-F(1)	93.1(1)	[92.6(1)]
M(2)-O(7)	1.894(1)	[1.965(1)]	O(2)-M(2)-F(1)	90.4(1)	[90.6(1)]
M(2)-O(2)	1.898(2)	[1.976(2)]	O(1)-M(2)-F(1)	175.6(1)	[174.7(1)]
M(2)-O(1)	1.905(2)	[1.989(2)]	O(3)-M(2)-O(9)	91.1(1)	[92.6(1)]
O(9)-H(9)	0.97(5)	[0.85(4)]	O(7)-M(2)-O(9)	171.7(1)	[171.5(1)]
			O(2)-M(2)-O(9)	86.6(1)	[86.9(1)]
			O(1)-M(2)-O(9)	88.7(1)	[89.7(1)]
			O(7)-M(2)-O(3)	92.1(1)	[92.4(1)]
			O(2)-M(2)-O(3)	176.8(1)	[177.8(1)]
			O(1)-M(2)-O(3)	89.5(1)	[89.3(1)]
			O(2)-M(2)-O(7)	90.5(1)	[88.3(1)]
			O(1)-M(2)-O(7)	83.7(1)	[83.6(1)]
			O(1)-M(2)-O(2)	92.6(1)	[92.9(1)]

TABLE IV—Continued

N(1)H ₄ tetrahedron ^a					
N(1)-H(2)	0.83(2)	10.84(2)}	H(4)-N(1)-H(2)	110(7)	{106(7)}
N(1)-H(4)	0.83(6)	10.85(6)}	H(3)-N(1)-H(2)	110(8)	{111(8)}
N(1)-H(3)	0.83(5)	10.81(5)}	H(1)-N(1)-H(2)	110(8)	{110(8)}
N(1)-H(1)	0.83(6)	10.82(6)}	H(3)-N(1)-H(4)	110(7)	{109(8)}
			H(1)-N(1)-H(4)	109(7)	{108(7)}
			H(1)-N(1)-H(3)	108(8)	{113(9)}
N(2)H ₄ tetrahedron ^a					
N(2)-H(5)	0.75(4)	10.85(4)}	H(7)-N(2)-H(5)	112(8)	{109(8)}
N(2)-H(7)	0.75(6)	10.84(5)}	H(6)-N(2)-H(5)	109(8)	{107(8)}
N(2)-H(6)	0.76(5)	10.86(4)}	H(8)-N(2)-H(5)	109(8)	{111(8)}
N(2)-H(8)	0.76(4)	10.83(5)}	H(6)-N(2)-H(7)	109(8)	{108(8)}
			H(8)-N(2)-H(7)	109(8)	{113(8)}
			H(8)-N(2)-H(6)	108(9)	{109(9)}

Anion-cation-anion bond angles

P(1)-O(1)-M(2)	131.8(1)	{129.6(1)}
P(2)-O(2)-M(2)	131.4(1)	{131.2(1)}
P(2)-O(3)-M(2)	138.8(1)	{134.5(1)}
P(1)-O(4)-M(1)	166.0(1)	{156.2(1)}
P(2)-O(5)-M(1)	135.9(1)	{131.5(1)}
P(2)-O(6)-M(1)	133.4(1)	{131.4(1)}
P(1)-O(7)-M(2)	151.2(1)	{152.3(1)}
P(1)-O(8)-M(1)	131.4(1)	{129.8(1)}
M(1)-O(9)-M(2)	131.0(1)	{127.1(1)}

^a Distances are relative to the maximum of electron density of the N-H bonding (see text).

TABLE V
VALENCE BOND ANALYSES^a OF (NH₄)_{0.88}(H₃O)_{0.12}AlPO₄(OH)_{0.33}F_{0.67}(AlPO₄-CJ2) AND
(NH₄)_{0.93}(H₃O)_{0.07}GaPO₄(OH)_{0.5}F_{0.5} (IN ITALICS)

Anions	Cations	P(1)	P(2)	M(1)	M(2)	H	Sum	Charge
O(1)		1.246	0.005	0.012	0.506	0.074	1.843	2
		1.244	0.003	0.013	0.500	0.095	1.855	
O(2)		0.006	1.212	0.013	0.519	0.138	1.888	2
		0.003	1.186	0.012	0.524	0.114	1.839	
O(3)		0.009	1.240	0.007	0.519	0.051	1.826	2
		0.007	1.227	0.009	0.524	0.042	1.808	
O(4)		1.221	0.012	0.717	0.006	0.042	1.998	2
		1.219	0.012	0.697	0.006	0.042	1.976	

TABLE V—Continued

Anions	Cations	P(1)	P(2)	M(1)	M(2)	H	Sum	Charge
O(5)		0.002	1.201	0.545	0.004	0.056	1.808	2
		<0.001	1.199	0.550	0.004	0.048	1.801	
O(6)		<0.001	1.159	0.686	0.006	0.051	1.902	2
		<0.001	1.154	0.710	0.006	0.073	1.943	
O(7)		1.251	<0.001	<0.001	0.518	0.064	1.833	2
		1.250	<0.001	0.002	0.530	0.049	1.831	
O(8)		1.159	0.003	0.642	0.006	0.054	1.864	2
		1.161	0.003	0.655	0.005	0.051	1.875	
O(9) ^b		0.023	0.041	0.534	0.525	0.025	1.148	2
		0.020	0.023	0.574	0.548	0.029	1.194	
O(9) ^c		0.023	0.041	0.534	0.525	0.960	2.083	2
		0.020	0.023	0.574	0.548	1.326	2.455	
F(1)		0.004	0.009	<0.001	0.494	0.160	0.667	1
		0.004	0.004	<0.001	0.466	0.161	0.635	
Sum		4.921	4.882	3.156	3.103	/	/	/
		4.911	4.810	3.222	3.113	/	/	
Charge		5	5	3	3	1	/	/

^a The bond valences were calculated using the model proposed by I.D. Brown (10) within a coordination sphere with radius 4 Å for each atom belonging to the framework. The parameter values used in the determination of the bond valences are taken from the Ref. (11).

^b Bond valence assuming one oxygen in O(9) alone.

^c Bond valence assuming one oxygen in O(9) linked to one hydrogen.

TABLE VI

d SPACING (Å) OF THE RESIDUE OF (NH₄)_{0.93}(H₃O)_{0.12} GaPO₄(OH)_{0.5}F_{0.5} AFTER ANNEALING AT 600°C UNDER NITROGEN.

<i>d</i> _{obs}	Int	<i>d</i> (GaPO ₄) ^a
5.09	12	
4.32	66	
4.13	100	4.13
3.83	55	
3.545	18	3.574
3.269	17	
2.984	26	
2.497	29	2.527
2.323	31	
2.141	18	2.155
2.079	13	2.063
1.695	11	
1.635	11	1.6401

^a *d* spacing taken from JCPDS File No. 31-0547.

nels along the *a* and *b* axes contain N(2)H₄⁺ ammonium groups.

Upon heating, AlPO₄-CJ2 begins to decompose at 280°C. At 450°C, after a 26.67% weight loss, the compound is quasi-amorphous. (NH₄)_{0.93}(H₃O)_{0.07}GaPO₄(OH)_{0.5}F_{0.5} begins to decompose at a lower temperature (200°C); a single step weight loss of 17.81% completed at 340°C could be assigned to the departure of NH₄F, NH₃, and H₂O (theoretical: 17.4%). The XRD pattern of the residue at 600°C exhibits broad peaks some of which correspond to the gallophosphate GaPO₄ (JCPDS File No. 31-0547). The X-ray thermodiffraction study of the residues is currently in progress. See Table VI.

A NMR study of the aluminophosphate is presented in part II (9).

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