

Hydrothermal synthesis and crystal structure of a novel layered fluorinated gallium phosphate intercalating 1,12-diaminododecane $\text{Ga}_4(\text{PO}_4)_4\text{F}_4 \cdot \text{N}_4\text{C}_{24}\text{H}_{60}$ (MIL-35)

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Received 22 May 2000; received in revised form 12 June 2000; accepted 26 June 2000

Abstract

$\text{Ga}_4(\text{PO}_4)_4\text{F}_4 \cdot \text{N}_4\text{C}_{24}\text{H}_{60}$ or MIL-35 is a new layered fluorinated gallium phosphate obtained by mild hydrothermal synthesis using 1,12-diaminododecane as structure-directing agent. It crystallizes in the triclinic space group $P1$, $a = 539.3(2)$ pm, $b = 981.3(7)$ pm, $c = 1928.5(7)$ pm, $\alpha = 80.67(6)^\circ$, $\beta = 88.78(5)^\circ$, $\gamma = 89.86(7)^\circ$, $V = 1006.9(9) \times 10^6$ pm³, $Z = 1$ and the refinements from single-crystal X-ray diffraction analysis converge to $R1(F) = 0.0622$ and $wR2(F^2) = 0.1346$ for 5044 reflections with $I > 2\sigma(I)$. The inorganic sheets, stacked along $[0\ 0\ 1]$ consist of GaO_4F_2 octahedra connected with PO_4 tetrahedra interleaved by 1,12-diaminododecane molecules. The angle formed by the inorganic layer and the diamine molecule is around 52° . © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydrothermal synthesis; Layered compound; Fluorinated gallium phosphate; X-ray structure determination

1. Introduction

The research of microporous compounds with novel three-dimensional architectures is of great interest because of their potential applications in the areas of catalysis, gas separation or ionic exchangers [1]. Besides the best-known porous aluminosilicates, i.e. zeolites, the aluminum or gallium phosphate families have been intensely studied and for instance, frameworks with very large openings have been reported for the aluminophosphate VPI-5 [2] or the gallophosphate cloverite [3]. This class of materials is usually prepared hydrothermally under mild conditions ($T = 100$ – 200°C , autogenous pressure) by using organic molecules (amine or tetra-alkylammonium cations) as structure-directing agents. In addition to the three-dimensional networks, numerous layered or chain-like structures have been produced. In these phases, the organic species is intercalated between the inorganic sheet or chain and ensures the cohesion of the solid via hydrogen bond interactions. Most of these compounds also differ by the P:M ($M = \text{Al}, \text{Ga}$) ratio which may vary from 1:1 to 2:1. For this compositional domain, there exists two-dimensional varieties with P:M

ratios corresponding to 1:1 [4–6], 5:4 [7], 4:3 [8–28], 3:2 [29–33] and 2:1 [34–38]. The different structures have been obtained by changing the nature of the organic template and the solvent (water, alcohol, etc.).

Fluorine is a supplementary parameter which can affect the formation of open-frameworks solids. Its use for the hydrothermal reaction was initially developed by Kessler [39] and a large number of fluorinated phosphates have been isolated for the last 10 years. The crystal chemistry of fluorinated gallium phosphates was mainly investigated since it exhibited a wide structural diversity. Frameworks containing extra-large pores delimited by 12- (TREN-GAPO [40]), 14- (DIPYR-GaPO [41]), 16- (ULM-5 [42], ULM-16 [43]), 18- (MIL-31 [44]) and 20-membered rings (cloverite [3]) and layered structures [45–50] have been obtained in this chemical system. In general, fluorine belongs to the inorganic framework: it is either directly linked to the gallium atoms (terminal or bridging position) or encapsulated into small cubic-shaped cavities (double 4-ring cage).

Recently, we focused our attention on the influence of the length of linear alkylendiamines for the formation of three-dimensional fluorinated gallium phosphates [51]. We observed that short C_n alkyl chains ($2 < n < 5$) induce frameworks with 10-membered rings (ULM-3, ULM-4) while longer ones ($6 < n < 8$) lead to frameworks with

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larger channels delimited by 16 polyhedra (ULM-5, ULM-16). Our last results indicated that the use of C₉ or C₁₀ alkylendiamine chains gave rise to a network with 18-ring channels [44]. Such long chain diamines as templates have been previously reported in the syntheses of layered aluminum phosphates [10,52] and we report in this paper the experiments carried out with the 1,12-diaminododecane molecule. We describe the synthesis and the crystal structure of layered fluorinated gallium phosphate Ga₄(PO₄)₄F₄·N₄C₂₄H₆₀ labeled MIL-35. The structure of the inorganic sheet presents a new atomic arrangement which was not encountered in the other lamellar phosphates up to now.

2. Experimental

2.1. Synthesis

MIL-35 was prepared by mild hydrothermal synthesis under autogenous pressure. The starting reactants were gallium oxyhydroxide (GaO(OH), obtained from the reaction of gallium metal with water at 220°C for 3 days), phosphoric acid (H₃PO₄, 85%, Prolabo), hydrofluoric acid (HF, 40%, Prolabo), 1,12-diaminododecane (H₂N(CH₂)₁₂NH₂, 98% Aldrich, noted DADD here) and desionized water. The mixture with the molar ratio 1Ga (0.713 g):1P (0.40 ml):1F (0.12 ml), 1DADD (1.388 g):40H₂O (5 ml) was placed in a Teflon-lined steel Parr autoclave at 180°C over 3 days. The pH was 3 at the beginning of the reaction and rose to 6 at the end. The resulting white powdered product was filtered off, washed with water and dried in air at room temperature overnight. The X-ray powder pattern which is typical of a lamellar solid shows intense Bragg peaks at very low angle ($d = 1902$ pm) together with their harmonic peaks at $d = 951$ and 634 pm (Fig. 1). A small amount of the precursor GaOOH is also observed with MIL-35.

2.2. Crystallography

A colorless platelet-shaped single crystal was isolated for the X-ray diffraction structural analysis. The X-ray data

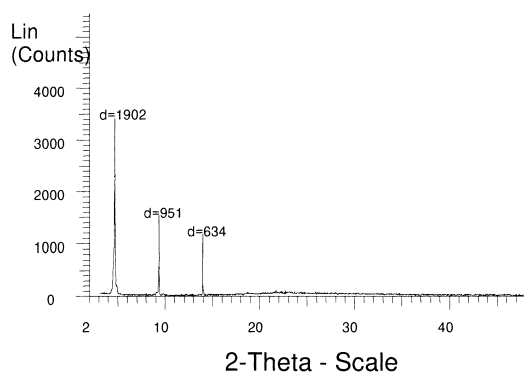


Fig. 1. X-ray diffraction pattern of MIL-35 showing the most intense Bragg peaks (pm).

were recorded at room temperature on a Siemens SMART three-circle diffractometer equipped with a CCD bidimensional detector (monochromated Mo K α radiation). The crystal-to-detector distance was 45 mm allowing for the data collection up to 60° (2θ). Slightly more than one hemisphere of data was recorded. The frames were collected with a scan width of 0.3° in an exposure time of 240 s. Crystal data and details of the data collection are given in Table 1. The structure was solved by direct method in the triclinic non-centric space group $P1$ (n°) and refined by full-matrix least-squares using the SHELX-TL package [53]. The gallium atoms were first located and all non-hydrogen atoms (P, C, O, N, C) positions were then revealed from the subsequent Fourier maps syntheses. Four fluorine atoms were placed on the sites bridging two gallium atoms from valence bond considerations [54]. The fluorine chemical analysis confirmed this point and gave four fluorine atoms for four GaPO₄ units (wt.% (F) = 4.78%, (P) = 7.85%, or F/P = 0.99 wt.%). For the final refinement, the hydrogen atoms of the diamine were constrained geometrically. The reliability factors, with anisotropic temperature factors, converge to $R1(F) = 0.0622$ and $wR2(F^2) = 0.1346$ for 5044 reflections $I > 2\sigma(I)$ with 510 parameters. The resulting atomic coordinates including isotropic temperature parameters, a selection of bond distances and angles are shown in Tables 2 and 3, respectively.

Table 1
Crystal data and details of the data collection for the MIL-35 structure

Identification code	MIL-35
Empirical formula	C ₂₄ H ₆₀ F ₄ Ga ₄ N ₄ O ₁₆ P ₄
Formula weight	1139.52
Temperature	296(2) K
Wavelength	71.073 pm
Crystal system	Triclinic
Space group	$P1$
Unit cell dimensions	$a = 539.3(2)$ pm; $\alpha = 80.67(6)^\circ$ $b = 981.3(7)$ pm; $\beta = 88.78(5)^\circ$ $c = 1928.5(7)$ pm; $\gamma = 89.86(7)^\circ$
Volume, Z	$1006.9(9) \times 10^6$ pm ³ , 1
Density (calculated)	1.879
Absorption coefficient	2.896 mm ⁻¹
$F(0\ 0\ 0)$	580
Crystal size	0.18 mm \times 0.05 mm \times 0.015 mm
Theta range for data collection	1.07 – 29.79°
Limiting indices	$-7 \leq h \leq 7$, $-13 \leq k \leq 9$, $-16 \leq l \leq 26$
Reflections collected	5866
Independent reflections	5044 [$R(\text{int}) = 0.0356$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5044/3/510
Goodness-of-fit on F^2	1.169
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0622$, $wR2 = 0.1345$
R indices (all data)	$R1 = 0.0957$, $wR2 = 0.1616$
Absolute structure parameter	0.05(4)
Extinction coefficient	0.024(2)
Largest diff. Peak and hole	1.162 and -1.217×10^{-6} e pm ⁻³

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{pm}^2 \times 10^7$) for MIL-35^a

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Ga(1)	9639(3)	9480(2)	8145(1)	12(1)
Ga(2)	13021(3)	14504(2)	8105(1)	16(1)
Ga(3)	6316(7)	11991(4)	8120(2)	11(1)
Ga(4)	16345(7)	16992(4)	8123(2)	12(1)
P(1)	8239(10)	14159(5)	9079(3)	9(1)
P(2)	4270(10)	9175(6)	9101(3)	14(1)
P(3)	8357(11)	14767(6)	7155(3)	10(1)
P(4)	14404(10)	19775(6)	7177(3)	15(1)
F(1)	9124(19)	11040(10)	8542(6)	11(3)
F(2)	13456(16)	16044(12)	8542(6)	20(3)
F(3)	9296(31)	7813(16)	7719(8)	57(5)
F(4)	13450(32)	12822(18)	7678(9)	60(5)
O(1)	4527(35)	8724(17)	9888(8)	18(4)
O(2)	14425(30)	18190(16)	7410(9)	11(3)
O(3)	6066(28)	13425(16)	8731(7)	7(3)
O(4)	8336(32)	13152(17)	7391(9)	17(4)
O(5)	14686(28)	20224(17)	6368(7)	24(4)
O(6)	8004(29)	13711(16)	9839(7)	22(4)
O(7)	6529(27)	8512(16)	8688(8)	9(3)
O(8)	8135(36)	15118(20)	6383(9)	28(4)
O(9)	10849(30)	15326(18)	7415(9)	17(4)
O(10)	10583(32)	13548(17)	8813(8)	15(3)
O(11)	11883(30)	8598(17)	8876(8)	14(4)
O(12)	6588(30)	10354(16)	7577(8)	12(3)
O(13)	4293(28)	10716(16)	8867(8)	13(4)
O(14)	11809(29)	10245(17)	7441(10)	18(4)
O(15)	18131(34)	15745(18)	8893(8)	15(4)
O(16)	16215(30)	15427(16)	7514(7)	13(4)
N(1)	8799(48)	7229(24)	10014(11)	37(6)
N(2)	13954(35)	16771(20)	6228(10)	16(4)
N(3)	9100(32)	11650(23)	6236(9)	21(5)
N(4)	3570(47)	12260(20)	9987(10)	31(6)
C(1)	8778(49)	16225(32)	10666(14)	31(6)
C(2)	6223(32)	15774(23)	10966(13)	26(6)
C(3)	6284(44)	14583(26)	11618(12)	23(5)
C(4)	3768(41)	14254(26)	11895(11)	32(7)
C(5)	3820(48)	13012(23)	12481(12)	27(6)
C(6)	11384(61)	12585(34)	12847(14)	36(7)
C(7)	11427(48)	21402(31)	3455(15)	32(7)
C(8)	18816(47)	20880(31)	3697(12)	42(8)
C(9)	18901(52)	19749(22)	4358(12)	40(7)
C(10)	16246(53)	19223(32)	4688(14)	43(8)
C(11)	16335(53)	18146(29)	5297(10)	41(8)
C(12)	13761(48)	17675(25)	5526(11)	16(5)
C(13)	9180(52)	12545(32)	5546(14)	35(7)
C(14)	11706(34)	13172(29)	5320(11)	33(7)
C(15)	11539(44)	14214(32)	4739(14)	39(8)
C(16)	4138(43)	14726(28)	4367(13)	33(7)
C(17)	3882(51)	15871(29)	3705(12)	33(6)
C(18)	6234(53)	16361(25)	3435(15)	49(9)
C(19)	6129(40)	7532(24)	12816(10)	29(6)
C(20)	8725(51)	7935(29)	12420(12)	35(7)
C(21)	8577(50)	9106(25)	11815(12)	32(6)
C(22)	975(49)	9648(25)	11575(12)	29(6)
C(23)	942(47)	10727(20)	10842(12)	27(6)
C(24)	3525(46)	11319(23)	10672(10)	19(5)

^a *U*(eq) is defined as one-third of the trace of the orthogonalized *U*_{ij} tensor.

Table 3

Bond distances and angles for MIL-35^a

Bond length (pm)	Angle (°)
Ga(1)–F(1)	83.7(11)
Ga(1)–O(14)	84(2)
Ga(1)–F(3)	96(2)
Ga(1)–O(11)	97(2)
Ga(1)–O(7)	10(2)
Ga(1)–O(12)	10(2)
Ga(2)–F(2)	86.4(12)
Ga(2)–O(9)	87(2)
Ga(2)–F(4)	97(2)
Ga(2)–O(10)	200(2)
Ga(2)–O(16)	216(2)
Ga(2)–O(3) ^b	222(2)
Ga(3)–F(4) ^c	190(2)
Ga(3)–F(1)	190.4(12)
Ga(3)–O(4)	197(2)
Ga(3)–O(3)	198(2)
Ga(3)–O(13)	204.6(13)
Ga(3)–O(12)	206(2)
Ga(4)–F(3) ^d	188(2)
Ga(4)–F(2)	191.2(9)
Ga(4)–O(2)	197(2)
Ga(4)–O(7) ^d	198.8(14)
Ga(4)–O(15)	202(2)
Ga(4)–O(16)	208(2)
P(1)–O(6)	146.2(14)
P(1)–O(10)	151(2)
P(1)–O(15) ^c	154(2)
P(1)–O(3)	159(2)
P(2)–O(13)	151(2)
P(2)–O(11) ^c	151(2)
P(2)–O(1)	152(2)
P(2)–O(7)	163.2(14)
P(3)–O(8)	148(2)
P(3)–O(16) ^c	153(2)
P(3)–O(9)	157(2)
P(3)–O(4)	158(2)
P(4)–O(2)	155(2)
P(4)–O(5)	155(2)
P(4)–O(14) ^c	157(2)
P(4)–O(12) ^d	158(2)
N(1)–C(1) ^f	147(3)
N(2)–C(12)	150(3)
N(3)–C(13)	147(3)
N(4)–C(24)	148(3)
C(1)–C(2)	152(3)
C(2)–C(3)	157(3)
C(3)–C(4)	146(3)
C(4)–C(5)	152(3)
C(5)–C(6) ^c	150(4)
C(6)–C(7) ^g	151(2)
C(7)–C(8) ^c	154(4)
C(8)–C(9)	155(3)
C(9)–C(10)	161(4)
C(10)–C(11)	145(3)
C(11)–C(12)	150(4)
C(13)–C(14)	152(3)
C(14)–C(15)	139(4)
C(15)–C(16) ^b	161(3)
C(16)–C(17)	157(4)

Table 3 (Continued)

Bond length (pm)	Angle (°)
C(17)–C(18)	142(4)
C(18)–C(19) ^h	152(2)
C(19)–C(20)	160(3)
C(20)–C(21)	150(3)
C(21)–C(22) ^b	144(4)
C(22)–C(23)	162(3)
C(23)–C(24)	152(3)
F(1)–Ga(1)–O(14)	97.3(7)
F(1)–Ga(1)–F(3)	165.9(6)
O(14)–Ga(1)–F(3)	91.4(7)
F(1)–Ga(1)–O(11)	95.1(6)
O(14)–Ga(1)–O(11)	102.6(7)
F(3)–Ga(1)–O(11)	93.8(7)
F(1)–Ga(1)–O(7)	91.2(5)
O(14)–Ga(1)–O(7)	162.7(7)
F(3)–Ga(1)–O(7)	77.6(6)
O(11)–Ga(1)–O(7)	91.6(6)
F(1)–Ga(1)–O(12)	79.0(6)
O(14)–Ga(1)–O(12)	91.4(7)
F(3)–Ga(1)–O(12)	89.8(7)
O(11)–Ga(1)–O(12)	165.4(6)
O(7)–Ga(1)–O(12)	75.4(6)
F(2)–Ga(2)–O(9)	97.0(6)
F(2)–Ga(2)–F(4)	165.8(6)
O(9)–Ga(2)–F(4)	93.7(8)
F(2)–Ga(2)–O(10)	96.0(5)
O(9)–Ga(2)–O(10)	100.0(7)
F(4)–Ga(2)–O(10)	91.3(7)
F(2)–Ga(2)–O(16)	80.2(5)
O(9)–Ga(2)–O(16)	91.9(6)
F(4)–Ga(2)–O(16)	90.2(7)
O(10)–Ga(2)–O(16)	167.9(7)
F(2)–Ga(2)–O(3) ^b	90.0(6)
O(9)–Ga(2)–O(3) ^b	167.9(6)
F(4)–Ga(2)–O(3) ^b	77.9(7)
O(10)–Ga(2)–O(3) ^b	89.0(6)
O(16)–Ga(2)–O(3) ^b	79.6(6)
F(4) ^c –Ga(3)–F(1)	176.0(8)
F(4) ^c –Ga(3)–O(4)	88.1(8)
F(1)–Ga(3)–O(4)	93.4(6)
F(4) ^c –Ga(3)–O(3)	85.9(7)
F(1)–Ga(3)–O(3)	97.8(6)
O(4)–Ga(3)–O(3)	94.0(6)
F(4) ^c –Ga(3)–O(13)	93.3(7)
F(1)–Ga(3)–O(13)	85.1(6)
O(4)–Ga(3)–O(13)	177.7(9)
O(3)–Ga(3)–O(13)	88.0(6)
F(4) ^c –Ga(3)–O(12)	97.7(7)
F(1)–Ga(3)–O(12)	78.6(6)
O(4)–Ga(3)–O(12)	90.8(6)
O(3)–Ga(3)–O(12)	174.1(8)
O(13)–Ga(3)–O(12)	87.1(6)
F(3) ^d –Ga(4)–F(2)	176.2(8)
F(3) ^d –Ga(4)–O(2)	89.7(7)
F(2)–Ga(4)–O(2)	93.1(6)
F(3) ^d –Ga(4)–O(7) ^d	82.2(6)
F(2)–Ga(4)–O(7) ^d	100.2(5)
O(2)–Ga(4)–O(7) ^d	0.0(7)
F(3) ^d –Ga(4)–O(15)	93.5(7)
F(2)–Ga(4)–O(15)	83.7(7)
O(2)–Ga(4)–O(15)	176.5(9)
O(7) ^d –Ga(4)–O(15)	89.2(7)
F(3) ^d –Ga(4)–O(16)	96.4(6)

Table 3 (Continued)

Bond length (pm)	Angle (°)
F(2)–Ga(4)–O(16)	81.2(6)
O(2)–Ga(4)–O(16)	89.6(6)
O(7) ^d –Ga(4)–O(16)	178.6(8)
O(15)–Ga(4)–O(16)	91.3(6)
O(6)–P(1)–O(10)	108.8(9)
O(6)–P(1)–O(15) ^c	111.1(9)
O(10)–P(1)–O(15) ^c	113.3(10)
O(6)–P(1)–O(3)	106.8(9)
O(10)–P(1)–O(3)	104.1(9)
O(15) ^c –P(1)–O(3)	112.4(9)
O(13)–P(2)–O(11) ^c	108.9(10)
O(13)–P(2)–O(1)	114.5(9)
O(11) ^c –P(2)–O(1)	108.7(10)
O(13)–P(2)–O(7)	108.1(8)
O(11) ^c –P(2)–O(7)	107.1(9)
O(1)–P(2)–O(7)	109.3(10)
O(8)–P(3)–O(16) ^c	109.4(10)
O(8)–P(3)–O(9)	111.8(11)
O(16) ^c –P(3)–O(9)	107.6(9)
O(8)–P(3)–O(4)	110.5(10)
O(16) ^c –P(3)–O(4)	110.2(9)
O(9)–P(3)–O(4)	107.3(10)
O(2)–P(4)–O(5)	113.5(9)
O(2)–P(4)–O(14) ^c	104.4(9)
O(5)–P(4)–O(14) ^c	110.0(10)
O(2)–P(4)–O(12) ^d	105.9(10)
O(5)–P(4)–O(12) ^d	111.5(8)
O(14) ^d –P(4)–O(12) ^c	111.2(9)
N(1) ^d –C(1)–C(2)	116(2)
C(1)–C(2)–C(3)	114(2)
C(4)–C(3)–C(2)	110(2)
C(3)–C(4)–C(5)	110(2)
C(6) ^c –C(5)–C(4)	117(2)
C(5) ^b –C(6)–C(7) ^g	117(2)
C(6) ^h –C(7)–C(8) ^c	113(2)
C(7) ^b –C(8)–C(9)	112(2)
C(8)–C(9)–C(10)	115(2)
C(11)–C(10)–C(9)	115(2)
C(10)–C(11)–C(12)	110(2)
C(11)–C(12)–N(2)	107(2)
N(3)–C(13)–C(14)	115(2)
C(15)–C(14)–C(13)	112(2)
C(14)–C(15)–C(16) ^b	115(2)
C(17)–C(16)–C(15) ^c	114(2)
C(18)–C(17)–C(16)	111(2)
C(17)–C(18)–C(19) ^h	114(2)
C(18) ^g –C(19)–C(20)	115(2)
C(21)–C(20)–C(19)	114(2)
C(22) ^b –C(21)–C(20)	113(2)
C(21) ^c –C(22)–C(23)	114(2)
C(24)–C(23)–C(22)	110(2)
N(4)–C(24)–C(23)	111(2)

^a Superscripts in this table indicate symmetry transformations used to generate equivalent atoms.

^b $x + 1, y, z$.

^c $x - 1, y, z$.

^d $x + 1, y + 1, z$.

^e $x, y + 1, z$.

^f $x, y - 1, z$.

^g $x, y - 1, z + 1$.

^h $x, y + 1, z - 1$.

3. Description of the structure

The crystal structure of MIL-35, as $\text{Ga}_4(\text{PO}_4)_4\text{F}_4 \cdot \text{N}_4\text{C}_{24}\text{H}_{60}$ is lamellar. The inorganic sheets consist of GaO_4F_2 octahedra connected with PO_4 tetrahedra and are stacked along $[0\ 0\ 1]$. The 1,12-diaminododecane molecules are interleaved between the sheets. In the layer, each gallium atom is six-fold coordinated with four oxygen atoms and two fluorine atoms and the resulting distorted gallium octahedra share to each other two edges (Fig. 2). Each common edge is composed of one oxygen and one fluorine. Within the octahedron, fluorine atoms are located in *trans* positions and the connection of gallium octahedra generates zig-zag chains running along $[0\ 1\ 0]$ with a *cis-trans* sequence. This type of chain geometry was not previously observed since only a straight edge-sharing octahedra chain was isolated in the layered gallium phosphates $\text{GaPO}_4(\text{OH}) \cdot 0.5\text{N}_2\text{C}_2\text{H}_{10}$ templated by ethylenediamine [4] (Fig. 3). In the $(0\ 0\ 1)$ plane, the gallium files are linked to each other by the phosphate groups. Two of the oxygen atoms of PO_4 units connect gallium atoms belonging to two adjacent octahedral files. The third oxygen atom corresponds to that of the common edge-sharing gallium octahedron and this anion is three-fold coordinated whereas all the other anions (O, F) of the gallium chain are two-fold coordinated. The corresponding Ga–O ($\langle \text{Ga}-\text{O} \rangle = 209$ pm) and P–O distances ($\langle \text{P}-\text{O} \rangle = 158$ pm) are longer than those observed for the Ga–O–P bonds ($\langle \text{Ga}-\text{O} \rangle = 196.1$ pm and $\langle \text{P}-\text{O} \rangle = 154.3$ pm). The Ga–F distances range from 184 to 197 pm and are identical to those found in pure gallium fluorides as in GaF_3 ($d_{\text{Ga}-\text{F}} = 189.2$ pm) [55] for instance. This case is slightly different in other fluorinated gallium phosphates templated by amines in which the fluorine is involved in hydrogen bond interactions with alkylammonium cations. This usually induces the lengthening of the Ga–F bond (≈ 200 pm). One oxygen atom of the phosphate

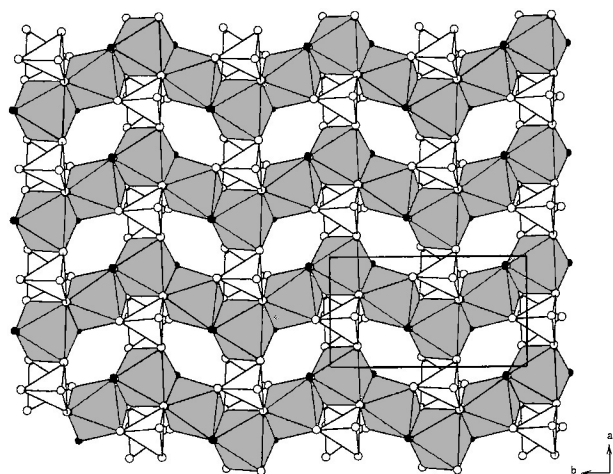


Fig. 2. View of the inorganic layer $[\text{Ga}_4(\text{PO}_4)_4\text{F}_4]^{4-}$ of MIL-35 along $[0\ 0\ 1]$. Black circles represent the fluorine atoms bridging the gallium atoms.

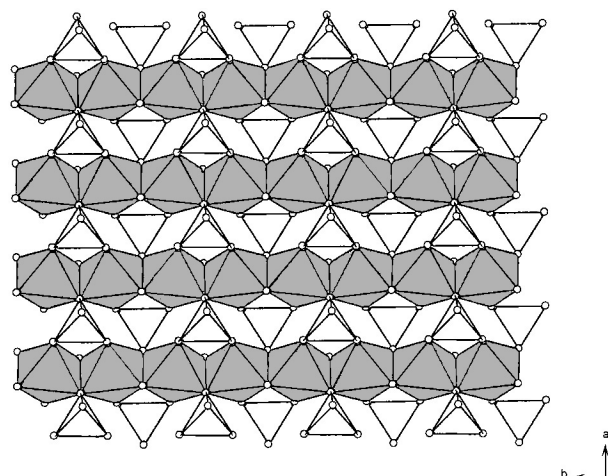
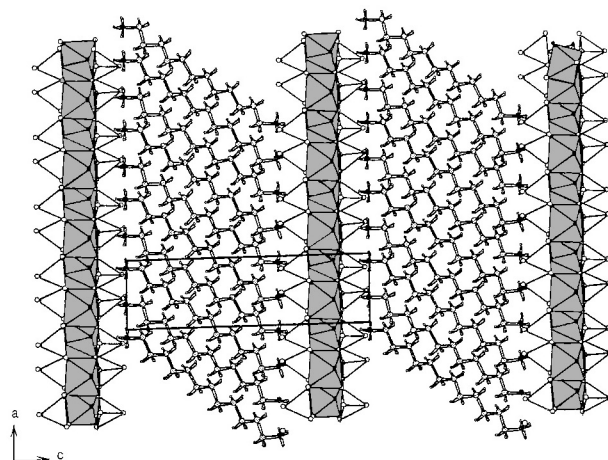
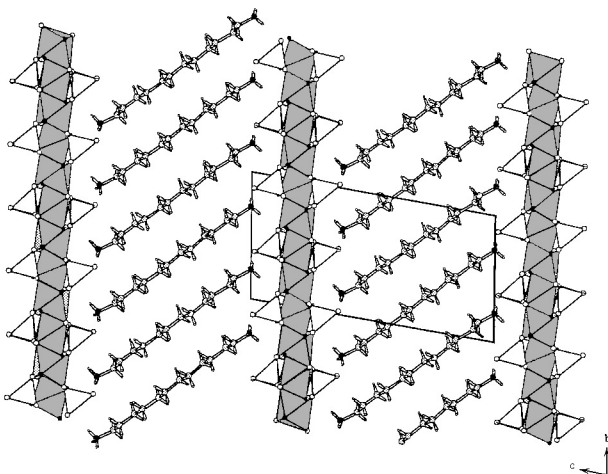


Fig. 3. View of the inorganic layer $[\text{GaPO}_4(\text{OH})]$ of the phosphate gallium $[\text{GaPO}_4(\text{OH}) \cdot 0.5\text{N}_2\text{C}_2\text{H}_{10}]$ showing the straight edge-sharing octahedra chain.



(a)



(b)

Fig. 4. View (a) along $[0\ 1\ 0]$ and (b) along $[1\ 0\ 0]$ of the structure of MIL-35 showing the inorganic layer intercalated by the 1,12-diaminododecane.

groups is terminal and points alternatively upward and downward from the layer.

The diamine is inserted between the inorganic sheet with an inclination angle of 52° (Fig. 4a and b). Such a situation was previously encountered in materials intercalated by long alkylendiamine molecules. For example, in α -zirconium [56] or aluminum phosphates [10], the diamines are not perpendicular to the inorganic layer but it has been calculated that the organic species makes an angle of 60° with the sheet. However, other AlPOs phases synthesized in alcoholic medium exhibit layered structures in which the diamine is strictly perpendicular to the sheet. This organic molecule orientation is observed in the UCSB- n ($n = 50$ – 53) [52] series and the fluorinated aluminophosphate ULM-13 [48] prepared with ethyleneglycol and ethanol, respectively. From these examples, the nature of the solvent (water or alcohol) used in the hydrothermal reaction seems to have a significant role for the organization of the diamine/sheet stacking. The ammonium groups of the diamine molecules strongly interact with the terminal oxygen of the phosphate units ($\langle O_{\text{terminal}} \cdots N \rangle = 275$ pm) and this explain the low bond valence calculated for these anions (around 1.3), instead of 2 for oxygen. The remaining oxygen atoms are less involved in hydrogen bond scheme with ammonium groups ($\langle O_{\text{bridging}} \cdots N \rangle = 290$ pm). In contrast, no interaction occurs between the fluorine and the diamine (shortest N–F distances > 398 pm).

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