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A new open-framework fluorinated gallium phosphate with large 18-ring channels (MIL-31)

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A new open-framework fluorinated gallium phosphate (MIL-31) containing the $Ga_9(PO_4)_9(H_2O)(OH)(OH,F)_4^{5-}$ anion was hydrothermally synthesized by using long alkyl chain diamines (C_9 and C_{10}) as structure-directing agents; its crystal structure is built up from hexameric units and exhibits large one-dimensional hexagonal channels delimited by 18-rings.

The search for new large pore materials has received much attention because of their potential applications in catalysis, ion exchange or molecular sieving. Historically, most of the porous solids are zeolite aluminosilicates and metal phosphates. Since the discovery of $AlPO_4$-*n*[1] in 1982, the syntheses of a large diversity of new open-framework structures[2] have been reported, many incorporating other elements such as B, Be, Ga, In, Sn, Sb or transition metals as well as oxyfluorides, sulfides, phosphonates, carboxylates, *etc*. Phosphate-based three-dimensional architectures contain pores larger than those usually observed in aluminosilicates. Whereas the pore size limit encountered in silicates corresponds to 14-membered rings (UTD-1[3]), some phosphates are characterized by extra large pore open-frameworks with 16-ring (Ga-ULM-5,[4] Ga-ULM-16,[5] Fe-ULM-15[6]), 18-ring (Al-VPI-5[7]), 20-ring (Al-JDF-20,[8] Ga-cloverite,[9] FePO,[10] GaPO[11]) and very recently 24-ring channels (Ni-VSB-1,[12] Zn-ND-1[13]). We now report here a new fluorinated gallium phosphate exhibiting a three-dimensional open-framework with 18-ring channels.

The MIL-31 compounds were synthezised under mild hydrothermal conditions by using either 1,9-diaminononane (DAN) or 1,10-diaminodecane (DAD) as structure-directing agents. There were prepared (180 °C, 3 days, autogenous pressure) from a mixture of gallium oxyhydroxide [GaO(OH), prepared from the reaction of gallium metal (4N, Rhône-Poulenc) with water at 200 °C for 24 h), phosphoric acid (H_3PO_4, 85%, Prolabo), hydrofluoric acid (HF, 48%, Prolabo), tripropylamine [NPr^n_3 (TPA), 98% Aldrich], 1,9-diaminononane [$H_2N(CH_2)_9NH_2$, 98% Aldrich] or 1,10-diaminodecane [$H_2N(CH_2)_{10}NH_2$, 97% Aldrich] and deionized water. Typically, the molar ratio was 1 Ga (0.356 g) : 1 P (0.16 ml) : 0.5 F (0.06 ml) : 80 H_2O (5 ml) : 0.4 TPA (0.25 ml) : 0.25 DAN (0.137 g) or 0.25 DAD (0.149 g). TPA was added in order to fix the reaction pH to between 3 and 4. Without TPA, only dense quartz-type $GaPO_4$ is formed. The resulting white thin needle-like crystals were filtered off, washed with water and dried at room temperature. The XRD patterns of both powdered samples were new and identical. With DAN, the compound was obtained with a yield of 90% together with a small amount of unreacted GaO(OH) whereas the yield is lower (70%) using DAD. However, only single crystals of the phase using DAD were suitable for X-ray structure determination† after hydrothermal treatment for one month. With DAN, the crystals were too small (even after a long reaction time). Only cell parameters can be extracted by using a conventional X-ray source diffractometer.‡

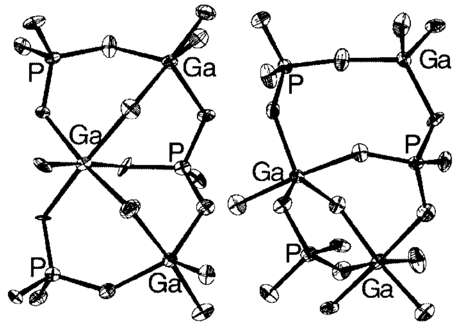

Fig. 1 Hexameric building units of MIL-31: $Ga_3(PO_4)_3(OH,F)_2$ of type I (left) and $Ga_3(PO_4)_3(OH)(H_2O)$ or type II (right).

The structure of MIL-31 consists of the connection of three crystallographically distinct building units (BU) composed of three phosphate groups and three gallium polyhedra (Fig. 1). Two of them are identical to that already observed in the ULM-*n* series[13] (denoted type I) built up from three PO_4 tetrahedra corner-sharing with one $GaO_4(OH,F)_2$ octahedron and two $GaO_4(OH,F)$ trigonal bipyramids. Within these hexameric units, the octahedron is in a central position and linked to the two $GaO_4(OH,F)$ trigonal bipyramids by corner-sharing *via* fluorine or hydroxy groups. These hexameric blocks are connected to each other whilst conserving strict Ga–P alternation in order to generate a sheet of composition $[Ga_6(PO_4)_6(OH,F)_4]$ in the *ab* plane (Fig. 2). In this layer, two adjacent units have opposite orientation, as already encountered in the 3D framework of ULM-16[5] or the 2D solid ULM-8.[14]

These hexameric-based layers are connected through a second type of BU (type II) with Ga_3P_3 stoichiometry. In this entity, the three phosphate groups share corners with three gallium polyhedra which exhibit three different coordinations:

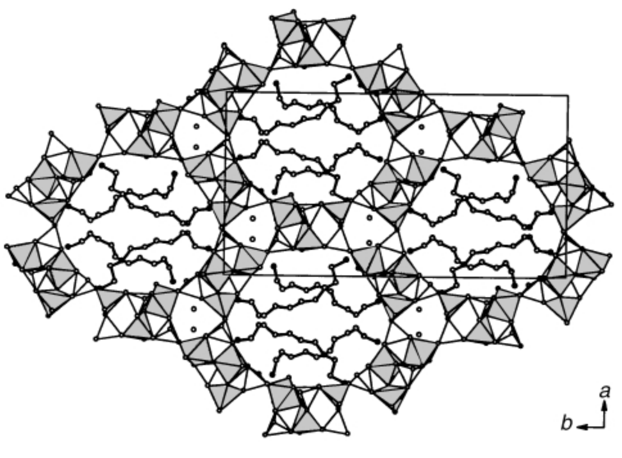

Fig. 2 View of the structure of MIL-31 along the 18-ring channels (along the *c* axis).

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GaO_4 tetrahedra, $GaO_4(OH)$ trigonal bipyramids and $GaO_4(OH)(H_2O)$ octahedra. The gallium bipyramidal unit is in the central position and has one common hydroxy group with the gallium octahedral unit. This BU is derived from TO_4-based 4-ring units (T = tetrahedral Ga or P species) forming infinite double-crankshaft chains as found in ULM-16.[5] In MIL-31, additional $GaO_4(OH)(H_2O)$ and PO_4 groups are connected to the 4-ring unit. This induces a change of the coordination of one of the GaO_4 tetrahedra to give a $GaO_4(OH)$ bipyramid. All the vertices of the gallium polyhedra are shared with the PO_4 polyhedra, except the terminal water molecule attached to the $GaO_4(OH)(H_2O)$ octahedron [Ga–OH_2 2.115(7) Å] pointing towards the channel centre. Such a situation was previously observed for the aluminophosphate VPI-5[15] in which one of the aluminium sites has an octahedral surrounding. This aluminium atom is at the center of the Al_3P_3 hexameric unit and is coordinated to four PO_4 groups and to two terminal water molecules.

Fluorine chemical analysis gave three fluorine atoms per $Ga_9(PO_4)_9$ unit which implies a statistical OH/F occupancy for the five observed Ga–X–Ga (X = OH or F) bridging positions. The ^{19}F NMR spectrum indicates only one signal at δ −93.8 (ref. $CFCl_3$) characteristic of bridging fluorine, but the spectral resolution precludes any assignment. However, in BU II the Ga–X distance ($<$Ga–X$>$ = 1.93 Å) is smaller than in BU I ($<$Ga–X$>$ = 2.00 Å). As only one peak is visible by ^{19}F NMR spectroscopy and given the measured fluorine content in the material, we can assume that the bridging site in BU II is only occupied by a hydroxy group and the fluorine would thus be located on the other bridging sites of the BU I.

The connection of these different building units generates a three-dimensional framework $[Ga_9(PO_4)_9(OH,F)_4(OH)(H_2O)]^{5-}$ composed of large hexagonal-shaped tunnels with 18- and 6-membered rings running along the *c* axis (Fig. 2). Two diprotonated diamines are inserted within the larger channels whereas two water molecules are trapped in the 6-ring channels. Each terminal ammonium group of the organic template interacts with anions of the framework *via* hydrogen bonds, with distances in the range 2.8–3.1 Å. These interactions occur between fluorine or hydroxy anions and one of the terminal ammonium groups of the template as already found in other phases of the ULM-*n* series.[14] The water molecules in the 6-ring channels interact with the ammonium groups *via* hydrogen bonding.

Besides the four positive charges from the organic molecules, an additional positive charge is required for the electroneutrality of the structure and might come from one H_3O^+ residing within the pore system. The pore opening diameter is *ca.* 12 Å but the presence of the terminal water of the gallium octahedron reduces thus to 10 Å along the *b* axis. The framework density calculated from the number of cations per 1000 Å^3 is 12.6 for MIL-*n* and is comparable to that found in the faujasite[16] structure (12.7) but lower than that observed in VPI-5 (14.2) which is also of 18-ring based topology.

The thermal behaviour of the DAN phase was characterized by X-ray diffraction and thermogravimetric analyses. The TG curve (Fig. 3) shows three major events. The first step (30–150 °C) is related to the removal of water (exptl: 4.30%; calc: 1.84%). The difference between the values would be due to the departure of five water molecules (calc: 4.50%) per $Ga_9(PO_4)_9$ unit, two found in the crystal structure analysis and three corresponding to adsorbed water. The second event (300–500 °C) can be assigned to the departure of the alkyldiamine and the observed experimental weight loss shows that the organic template is partly removed from the framework (exptl: 10.51%; calc: 16.51%). Above 600 °C, the weight loss is continuous and corresponds to 6.61% at 1000 °C. The XRD diagrams show clearly that the resulting structure is collapsed and transforms into dense $GaPO_4$ (high cristobalite). The weight loss can be assigned by assuming the removal of hydroxy groups and fluorine (exptl: 6.61%; calc: 4.67%) and additional organic template.

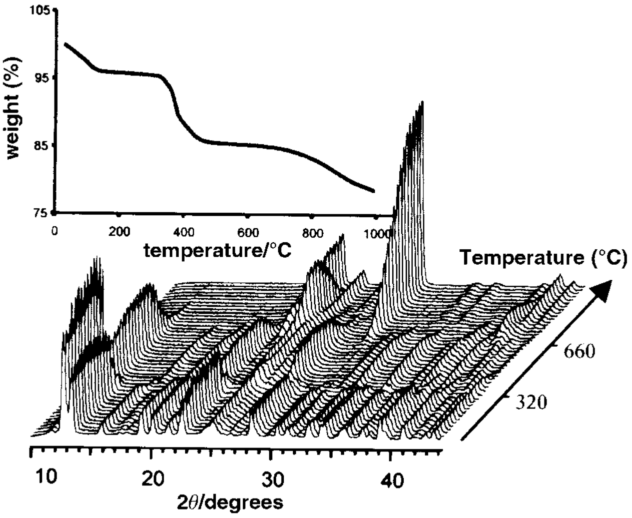

Fig. 3 Evolution of X-ray diffraction powder patterns as a function of temperature (30–1000 °C under air) and TG curve of MIL-31 (2 °C min^{-1} under N_2).

Notes and references

† *Crystal data* for MIL-31(DAD): $Ga_9(PO_4)_9F_3(OH)_2(H_2O)\cdot N_4C_{20}H_{52}\cdot 2H_2O$, M = 1975.93, orthorhombic, space group $Pca2_1$, μ = 4.549 mm^{-1}, $R1$ = 0.0624, $wR2$ = 0.1066 [for 8228 reflections with $I > 2\sigma(I)$], a = 17.4941(1), b = 32.3930(4), c = 10.0749(2) Å, V = 5709.3(1) Å^3, T = 293(2) K, Z = 4, 38201 reflections measured/13247 independent (R_{int} = 0.1030). Data collection was performed on a SMART three-circle diffractometer equipped with a CCD area detector (Mo-Kα radiation). The alkyldiamine molecules were refined with geometrical restraints. All atoms except for carbon and nitrogen were refined anisotropically. CCDC 182/1616. See http://www.rsc.org/suppdata/cc/b0/b001948h/ for crystallographic files in .cif format.

‡ *Crystal data* for MIL-31(DAN): orthorhombic, a = 17.4442(3), b = 32.1242(4), c = 10.1037(2) Å, V = 5661.921(2) Å^3. Elemental analysis: calc. for $Ga_9P_9O_{41}F_3N_4C_{18}H_{56}$: P, 14.33; F, 2.62; N, 2.87; C, 11.09. Found: P, 12.35; F, 2.54; N, 2.63; C, 9.78%.

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