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Hydrothermal synthesis and *ab initio* structure determination from powder data of a new three-dimensional mixed valence oxyfluorinated titanium phosphate with an open structure: $Ti^{III}Ti^{IV}F(PO_4)_2{\cdot}2H_2O$ or MIL-15

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$Ti^{III}Ti^{IV}F(PO_4)_2{\cdot}2H_2O$ (MIL-15) has been prepared hydrothermally (3 days, 483 K, autogenous pressure) in the presence of an organic base (diazabicyclo[2.2.2]octane). The structure of this compound has been determined *ab initio* from powder diffraction data and has been refined in the monoclinic space group: $P2_1/n$ (no. 14); the unit cell is $a = 10.935(1)$, $b = 14.447(1)$, $c = 5.105(1)$ Å, $\beta = 90.50(1)°$ and $V = 806.5(1)$ Å^3, $Z = 4$. Its three-dimensional network, built up from corner sharing TiX_6 octahedra ($X = F$, O, H_2O) and tetrahedral PO_4 groups, delimits seven-membered ring channels along the *c*-axis. The two crystallographically independent titanium atoms have different oxidation states (+III and +IV) and are connected *via* fluorine atoms while two water molecules are bound to the trivalent titanium atoms. Thermal decomposition of MIL-15 in two steps is described. Structural correlations with other titanium phosphates are presented.

1 Introduction

Since 1992, our group has been developing a series of oxyfluorinated metallophosphates (labelled ULM-*n*).[1] From the study of the relation between chemical parameters and the structure of alumino- and gallo-phosphates, an hypothesis for a mechanism of formation of these compounds was proposed, which suggested that the synthesis of metallophosphates with M = 3d transition element was possible.[1,2] Several oxyfluorinated compounds containing vanadium or iron as the metal were then discovered.[3–10] However, very few results have been published concerning tetravalent elements.

Recently, a series of oxyfluorinated zirconium phosphates have been structurally determined, some of them exhibiting three-dimensional structures with an open framework.[11–13] For the titanium phosphate family, despite the fact that these compounds have received considerable interest in recent decades, only the structural characterisation of dense phases obtained by high temperature synthesis like the KTP or $MTi_2(PO_4)_2$ (M = Li, Na, *etc.*) family of compounds have been reported.[14–16] In addition, very few compounds with open structures have been structurally determined up to now: the layered α- and γ-TiP compounds discovered in the 1970s,[17–18] and, more recently, three other two dimensional solids of formula $TiO(OH)(H_2PO_4){\cdot}2H_2O$, $Ti_2O_3(H_2PO_4){\cdot}2H_2O$ and β-$Ti(PO_4)(H_2PO_4)$, (an anhydrous form of γ-TiP).[19–21]. Furthermore, three new three-dimensional titanium phosphates with an open structure have been synthesised recently and characterised by Poojary *et al.*[22]: $Ti_3(PO_4)_4(H_2O)_2{\cdot}NH_3$, $Ti_2O(PO_4)_2{\cdot}2H_2O$ (ρ-TiP) and $(NH_4)[(Ti_2O_3)(HPO_4)_2(PO_4)_2]$.

Our group has initiated a systematic study of the titanium system and we recently reported the first two layered oxyfluorinated titanium phosphates: MIL-6 (MIL for Material Institut Lavoisier).[23] We present here the synthesis and the *ab initio* structure determination of a new three-dimensional, mixed valence titanium fluorophosphate with an open structure: $Ti^{III}Ti^{IV}F(PO_4)_2{\cdot}2H_2O$.

2 Experimental

The title compound was hydrothermally synthesised from a solution of 1 ml of dilute $TiCl_3$ and HCl (Aldrich 1.9 mol l^{-1}, molar ratio 1 : 1), 0.13 ml of aqueous H_3PO_4 (Prolabo Normapur 85%), 0.10 ml of aqueous HF (Prolabo Normapur 48%), 215 mg of diazabicyclo[2.2.2]octane (Aldrich 98%) and 3.75 ml of H_2O. The mixture was placed without stirring in a Teflon-lined steel autoclave under autogenous pressure for 3 days at 483 K; the pH increased from 1 to 2 during the reaction. The resulting dark purple powder, characteristic of the presence of trivalent titanium, was washed with demineralised water and dried at room temperature.

TGA experiments were performed with a TA-Instrument type 2050 analyser under oxygen flow. The different steps of the decomposition leading to an amorphous solid are described in the discussion, with the correlative results of thermodiffractometry.

The IR spectrum of the title compound (Fig. 1) clearly showed the presence of vibrational bands characteristic of phosphate groups around 1000 cm^{-1}; the absence of any vibrational band around 1450 cm^{-1} ruled out the presence of ammonium groups inside the structure.

Elemental analysis gave ratios P/Ti and F/Ti, respectively, of 0.95 and 0.65 (theoretical values: 1 and 0.5); only traces of

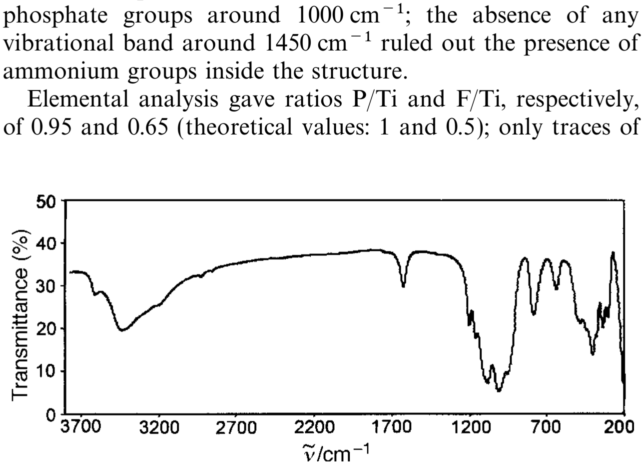

Fig. 1 IR spectrum of MIL-15.

carbon and nitrogen were detected, confirming the absence of any organic cation within the compound. The density measurement, performed on a Micromeretics apparatus, Accupyc 1330, gave $D_c = 2.90(2)$ g cm^{-3} (theoretical value 2.81 g cm^{-3}). These analyses confirmed the formula deduced from the structure determination: $Ti^{III}Ti^{IV}F(PO_4)_2 \cdot 2H_2O$.

3 Structure determination

All attempts to obtain crystals of sufficient size for single crystal X-ray diffraction failed. In fact, even if some crystals could be mounted on glass fibres, the thinness of the crystals (1–5 µm) ruled out any structure determination from single crystals. Therefore, an *ab initio* structure determination from X-ray powder data was performed. The pattern of MIL-15 showed a preferred orientation effect due to the size and the shape of the crystallites. Therefore, to minimise this effect, the powder was pulverised with a 'Mac Crone' grinder in ethanol (Prolabo, 95%), dried at 373 K and then side loaded in the sample-holder.

The powder diffraction diagram was collected on a D5000 Siemens diffractometer and was indexed with the Dicvol91 program.[24] A monoclinic solution was found with satisfactory figures of merit [M(20)/F(20) = 55 and 111 (0.0046, 39)]; systematic absences were consistent with the space group $P2_1/n$ (no. 14) and the indexed powder pattern is reported in Table 1.

The pattern matching was performed with Fullprof 97,[25] and the structure was solved by the direct method using Sirpow92.[26] The final Rietveld refinement, also made by Fullprof, using 931 F_{obs}, was carried out in the angular range 2θ 15.8–80° (owing to a strong preferred orientation, the two first reflections were excluded to improve the refinement). Refinement involved the following parameters: one scale factor, 45 atomic coordinates, one overall isotropic temperature factor, one zero point and four cell parameters, three half-width parameters, four asymmetry factors, two parameters to define the θ-dependent pseudo-Voigt profile shape function, five coefficients to describe the functional dependence of the background and one preferred orientation factor. Soft distances constraints were applied for the Ti–X (X = O, F, H_2O) and P–O interatomic distances. Details of the structure determination are summarised in Table 2.

Table 1 Indexed powder pattern of MIL-15[a]

hkl	$2\theta_{obs}$	$2\theta_{calc}$	d_{hkl}/Å	Intensity
0 2 0	12.231	12.242	7.22	100
1 2 0	14.673	14.685	6.03	70
2 0 0	16.177	16.198	5.47	4
2 1 0	17.318	17.327	5.11	1
0 1 1	18.393	18.417	4.813	1
1 0 −1	19.089	19.106	4.641	1
1 0 1	19.225	19.236	4.610	4
1 3 0	20.104	20.078	4.419	8
2 2 0	20.339	20.354	4.359	44
1 2 −1	22.739	22.754	3.905	3
2 1 −1	24.514	24.519	3.627	10
0 4 0	24.601	24.614	3.614	20
0 3 1	25.380	25.405	3.503	3
1 3 −1	26.630	26.652	3.342	4
1 3 1	26.760	26.747	3.330	5
2 2 1	26.957	26.965	3.304	10
3 2 0	27.357	27.384	3.254	4
2 4 0	29.593	29.618	3.014	24
3 0 −1	29.968	29.973	2.979	3
0 4 1	30.265	30.288	2.948	7
2 3 1	30.334	30.361	2.941	10
1 4 1	31.425	31.438	2.843	1
1 5 0	31.980	32.011	2.793	6
3 2 −1	32.467	32.486	2.754	1
3 2 1	32.726	32.723	2.734	2

[a] Indexing based on parameters obtained by Rietveld refinement (Table 2).

Table 2 Crystallographic data for MIL-15

M/g mol^{-1}	341
D_c/g cm^{-3}	2.81
Symmetry	Monoclinic
Space group	$P2_1/n$ (no. 14)
Z	4
a/Å	10.935(1)
b/Å	14.447(1)
c/Å	5.105(1)
β/°	90.50(1)
V/Å^3	806.5(1)
λ(Cu-Kα_1, Kα_2)/Å	1.54059, 1.54439
Range 2θ/°	7–35, 35.02–80
Time per step/s	30 (range 1) and 60 (range 2)
Step size/°	0.02
Excluded area 2θ/°	7.00–15.80
Total no. of reflections	981
Total no. points	3143
No. structural parameters	47
No. profile parameters	20
No. atoms refined	15
No. distance constraints	20
R_p (%)	11.4
R_{wp} (%)	14.6
R_{Bragg} (%)	9.0
R_F(%)	5.6

The final agreement factors are satisfactory: $R_p = 11.4\%$, $R_{wp} = 14.6\%$ and $R_{Bragg} = 9.0\%$, $R_F = 5.6\%$. The final Rietveld plot of the refined structure is shown in Fig. 2. Atomic coordinates are reported in Table 3 while bond distances and angles are given in Table 4.

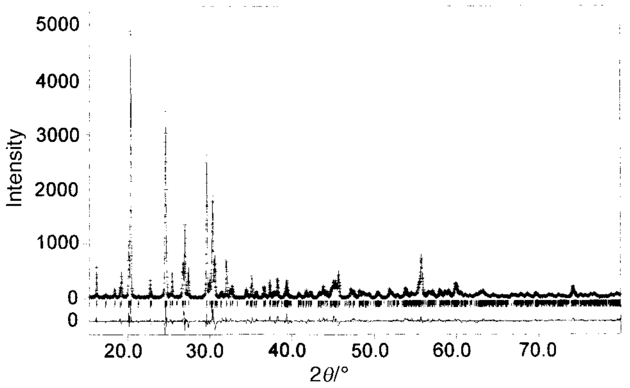

Fig. 2 Final Rietveld plot of MIL-15.

Table 3 Atomic coordinates for MIL-15[a]

Atom	*x*	*y*	*z*
Ti1	0.8130(4)	0.0380(3)	0.263(1)
Ti2	0.5490(5)	0.1690(3)	−0.496(1)
P1	0.6540(6)	−0.0240(5)	−0.239(2)
P2	0.9650(6)	0.1210(4)	−0.244(2)
F	0.686(1)	0.133(1)	0.273(3)
O1	0.568(1)	0.055(1)	−0.246(3)
O2	0.865(1)	0.111(1)	−0.054(3)
O3	0.753(1)	−0.025(1)	0.569(3)
O4	0.936(1)	−0.046(1)	0.219(3)
O5	0.716(1)	−0.030(1)	0.032(3)
O6	0.905(1)	0.122(1)	−0.509(3)
O7	0.567(1)	−0.109(1)	−0.255(4)
O8	0.549(1)	0.292(1)	0.293(3)
Ow1	0.672(1)	0.241(1)	−0.220(3)
Ow2	0.400(1)	0.197(1)	−0.251(3)

[a] Overall thermal isotropic factor: 0.55(1) Å^2

Table 4 Interatomic distances (Å) and angles (°) for MIL-15

Ti1–F	1.95(1)	Ti1–O4	1.82 (1)	P1–O1	1.48(1)	P1–O5	1.54(2)
Ti1–O2	2.01(2)	Ti1–O5	1.86(2)	P1–O3	1.46(2)	P1–O7	1.56(1)
Ti1–O3	1.93(2)	Ti1–O6	1.95(1)	P2–O2	1.48(2)	P2–O6	1.50(2)
Ti2–F	1.98(1)	Ti2–O8	2.08(1)	P2–O4	1.54(1)	P2–O8	1.57(1)
Ti2–O1	2.09(1)	Ti2–Ow1	2.21(2)				
Ti2–O7	1.98(2)	Ti2–Ow2	2.10(1)				
F–Ti1–O2	82(1)	O2–Ti1–O6	91(1)	O1–P1–O3	117(2)	O3–P1–O5	106(2)
F–Ti1–O3	94(1)	O3–Ti1–O4	92(1)	O1–P1–O5	110(2)	O3–P1–O7	114(2)
F–Ti1–O4	174(1)	O3–Ti1–O5	94(1)	O1–P1–O7	103(2)	O5–P1–O7	106(2)
F–Ti1–O5	89(1)	O3–Ti1–O6	89(1)	O2–P2–O4	113(1)	O4–P2–O6	112(1)
F–Ti1–O6	85(1)	O4–Ti1–O5	89(1)	O2–P2–O6	106(2)	O4–P2–O8	98(1)
O2–Ti1–O3	176(1)	O4–Ti1–O6	96(1)	O2–P2–O8	116(1)	O6–P2–O8	111(1)
O2–Ti1–O4	92(1)	O5–Ti1–O6	174(1)				
O2–Ti1–O5	86(1)						
F–Ti2–O1	95(1)	O1–Ti2–Ow2	82(1)				
F–Ti2–O7	89(1)	O7–Ti2–O8	93(1)				
F–Ti2–O8	85(1)	O7–Ti2–Ow1	177(1)				
F–Ti2–Ow1	92(1)	O7–Ti2–Ow2	89(1)				
F–Ti2–Ow2	176(1)	O8–Ti2–Ow1	86(1)				
O1–Ti2–O7	96(1)	O8–Ti2–Ow2	98(1)				
O1–Ti2–O8	171(1)	Ow1–Ti2–Ow2	90(1)				
O1–Ti2–Ow1	86(1)						

4 Discussion

This structure is three-dimensional. The framework is made of corner-sharing titanium octahedra and tetrahedral phosphate groups; the dark purple colour of the compound indicates the presence of trivalent titanium and valence bond calculations show that Ti1 is tetravalent and Ti2 trivalent. Bridging fluorine atoms connect the two titanium atoms to build dimeric mixed valence titanium units; these units are then linked *via* phosphate groups to lead to three-dimensionality of the framework. This leads to an open structure made up of channels along the *c*-axis circumscribed by seven-membered rings (Fig. 3). Two independent water molecules are bound to the trivalent titanium atoms and point toward the channels.

The titanium atoms exhibit different environments (Fig. 3): the tetravalent titanium atom (Ti1) is surrounded by five bridging oxygens and one fluorine atom while the trivalent titanium atom (Ti2) is surrounded by three bridging oxygens, one fluorine atom and two terminal water molecules. Interatomic distances and angles are in good agreement with those usually reported for titanium phosphates: 1.46–1.57 Å for P–O distances and 1.82–2.08 Å for Ti–O distances. For the water molecules, the interatomic distances are 2.10 and 2.21 Å which are reasonable for Ti^{III}–Ow distances. The Ti–F distances are also well defined at 1.95 and 1.98 Å close to Ti–F distances (for bridging fluorine atoms) reported in the crystal structures of TiF_4 and TiF_3.[27–28]

The structure can also be described in terms of building units with two different trivalent titanium and tetravalent titanium SBU (secondary building units): $Ti^{III}{}_2F_2O_2(H_2O)_4(PO_4)_2$ and $Ti^{IV}{}_2F_2O_6(PO_4)_2$ (Fig. 4). These SBU are linked through Ti–O–P and Ti–F–Ti connections to produce an array of seven-membered ring channels along the [001] axis.

The short distance between the oxygens of terminal water molecules which point toward the tunnels (2.67 Å) indicates absence of porosity for this compound. However, the departure

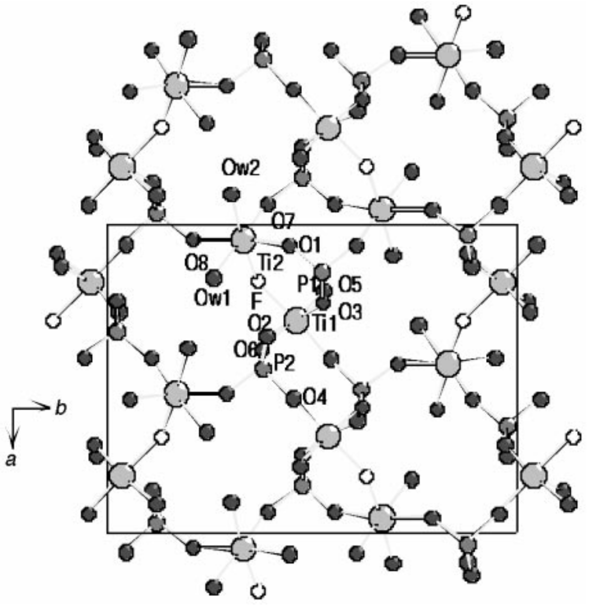

Fig. 3 Ball and stick representation along [001] of MIL-15 with atom labelling as in Table 3; fluorine atoms are represented as empty circles.

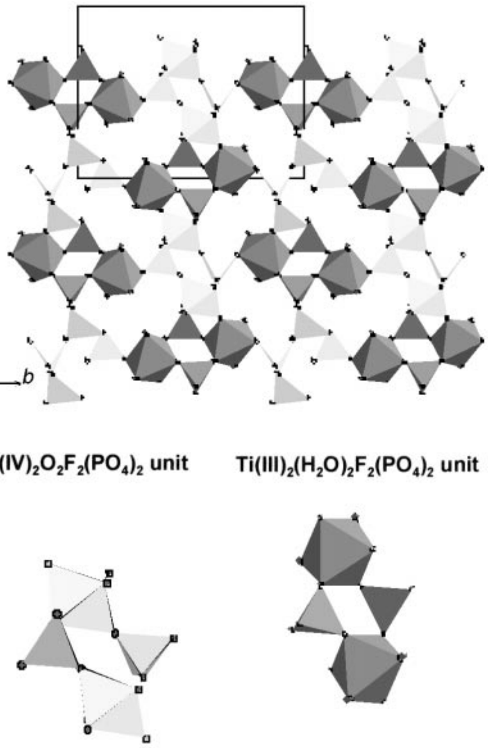

Fig. 4 View of the MIL-15 structure in terms of Ti^{III} and Ti^{IV} SBU (see text) represented as inserts below the figure.

of a water molecule might allow the inclusion of small guest molecules.

One can compare this structure with $Ti^{IV}_2O(PO_4)_2{\cdot}2H_2O$ (ρ-TiP);[22] this phase also has a three-dimensional framework and shows six and eight membered-ring channels along the *a*-axis instead of the seven-membered ring channels in our case. However, the SBU of both structures are topologically identical. For a better comparison, these SBU can be assimilated to a spin in the direction of the long diagonal of the rhombic vacancy (ANNNI model: antiferromagnetic next nearest neighbours interaction) [Fig. 5(c)]. Then, ρ-TiP corresponds to a 'ferromagnetic' arrangement [Fig. 5(a)] and MIL-15 to a 'canted antiferromagnet' [Fig. 5(b)]. A 60° rotation of one half of the SBU allows the transformation from one structure to the other. The rotation in ρ-TiP changes the number of polyhedra forming the tunnel. The eight-membered channels lose one polyhedron whereas the six-membered ones accept a seventh polyhedron to give the MIL-15 structure. The transformation can be summarised by the equation: 8-T (4 oct+4 t)+6-T (4 oct+2 t)=2×7-T (4 oct+3 t) in which n-T, oct and t represent the number of polyhedra limiting the tunnel, octahedra and tetrahedra respectively.

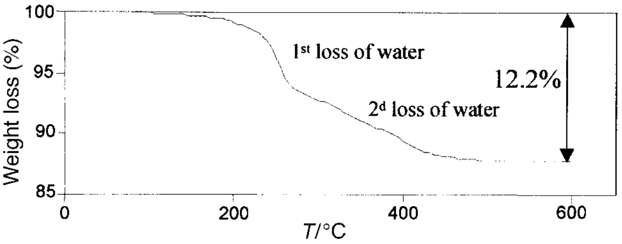

Fig. 6 Thermogravimetric analysis of MIL-15 (under O_2 flow).

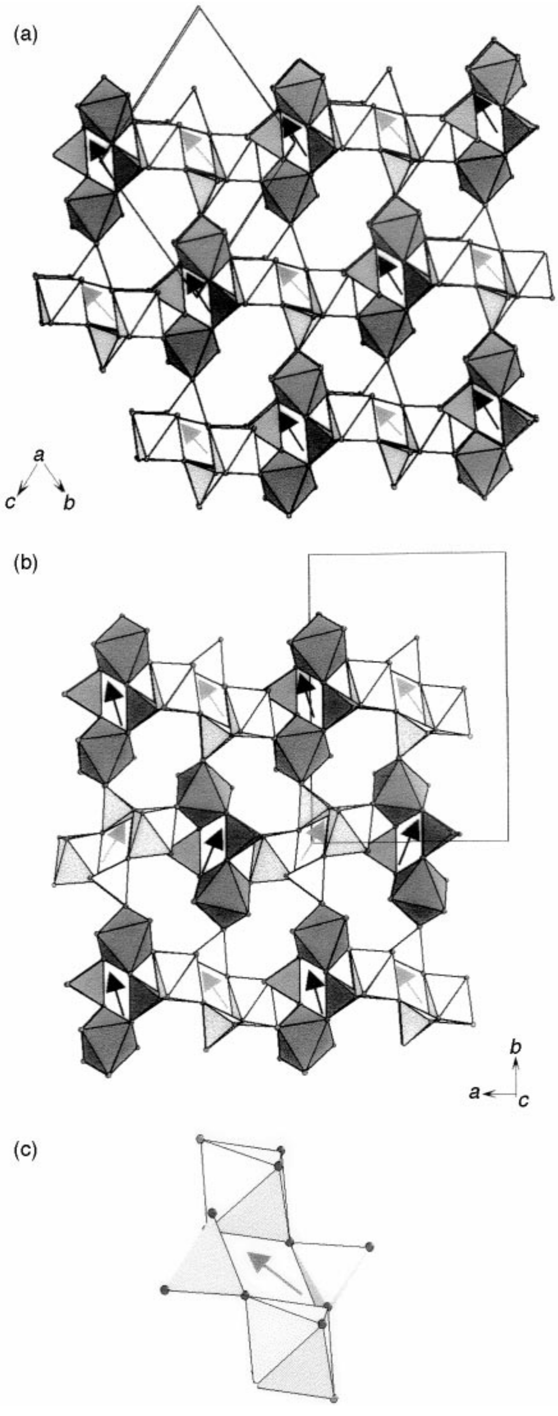

Fig. 5 ρTiP and MIL-15 description (ANNNI model): (a) ρ-TiP, (b) MIL-15, (c) MIL-15 SBU represented using the ANNNI model.

This rotation and the passage from ρ-TiP to MIL-15 can shed some light on the structure of π-TiP, another titanium phosphate reported by Bortun *et al.*,[29] with the same formula as ρ-TiP. Its low crystallinity did not permit any structure determination but the cell parameters proposed are close to those of MIL-15; in addition, this compound had an X-ray diffractogram very similar to that of our compound. Therefore, MIL-15 and π-TiP can be considered as isostructural, the only difference would arise from the mixed valence and the presence of fluorine atoms in our case.

The thermal evolution of MIL-15 was performed using TGA and X-ray thermodiffractometry. A first TGA showed a weight loss of 12.2% in two steps between 200 and 500 °C (Fig. 6) larger than the loss of the water molecules alone (% theoretical loss=10.5%); the white colour of the calcined (under oxygen atmosphere) residue, cooled to room temperature, indicated an irreversible $Ti^{III} \rightarrow Ti^{IV}$ oxidation on heating. The first loss was reversible and a second TGA experiment performed on the product calcined for a few hours at 300 °C, and cooled to room temperature, showed upon heating a weight loss of 10.0% corresponding to two water molecules. Therefore, during the first step of calcination (under an oxygen atmosphere), MIL-15 loses one water molecule and one HF molecule while the trivalent titanium atoms are oxidised with the departure of fluorine atoms; the latter are simultaneously replaced by oxygen atoms. Then, the initial 12.2% weight loss would correspond to removal of water and HF and the weight difference corresponding to the replacement of fluorine atoms by oxygen atoms (theoretical loss: 11.45%). The latter point was confirmed by an EDX analysis, performed using a JEOL 5800 LV scanning microscope, on the compound calcined for a few hours at 300 °C, which showed only residual traces of fluorine. The compound calcined at 600 °C is amorphous. From TGA experiments, the decomposition of MIL-15 can be summarised as follows:

$$Ti^{III}Ti^{IV}F(PO_4)_2{\cdot}2H_2O \xrightarrow[\substack{-HF,\ -H_2O\\ +O}]{300\,^{\circ}C}$$

$$Ti^{IV}_2O(PO_4)_2{\cdot}H_2O \xrightarrow[-H_2O]{500\,^{\circ}C} \text{amorphous}$$

X-Ray thermodiffractometry (Fig. 7) was applied to MIL-15 to study its dehydration. Initially, between 100 and 300 °C, slight variations of the peak intensities, are observed but the structure is, on the whole, retained up to 380 °C. Between 300 and 400 °C, an irreversible modification of the pattern occurs, with a new diagram characteristic of $Ti^{IV}_2O(PO_4)_2{\cdot}H_2O$ and different from π-TiP. It can however be indexed in a cell very

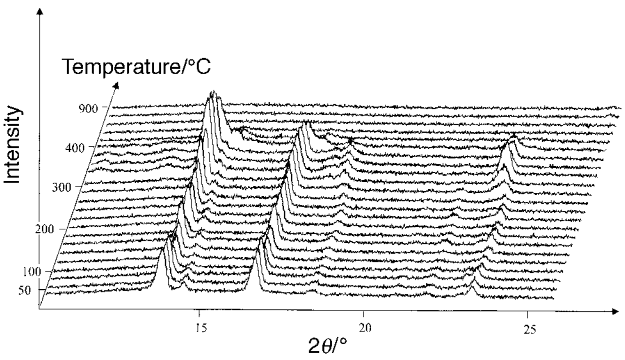

Fig. 7 X-Ray thermodiffractogram of MIL-15 under air.

close to that of MIL-15 with a doubling of the *c*-parameter (10.18 *cf.* of 5.11 Å).

The two water molecules belong to the Ti^{III} octahedra with Ti–Ow distances of 2.10 (Ow2) and 2.21 (Ow1) Å. It may be proposed that the first loss corresponds to the departure of Ow1. This implies a modification of the Ti–O distances and particularly a strengthening of the Ti–Ow2 bound followed with an alternate reorientation of this bond occurring between two cells leading to a doubling of the *c*-parameter. The low crystallinity of this compound unfortunately ruled out any further structural characterization.

We have noted that the titanyl linkages occurring usually in similar structures where titanium(IV) dimers are present, have been replaced by bridging fluorine atoms in the structure of MIL-15. This phenomenon has already been observed in the synthesis of other metallophosphates. For example, ULM-9[30] which has been synthesised both with vanadium(IV) and gallium(III) exhibits vanadyl linkages in the vanadium(IV) compound and bridging fluorine in the gallium(III) phase.

Furthermore, while the structure of π-TiP could not be solved from powder data owing to its low crystallinity, the presence of fluorine probably increases the crystallinity of MIL-15 sufficiently allowing structure determination.

MIL-15 is an example of a rare three-dimensional titanium phosphate with an open structure and one of the first three-dimensional mixed valence oxyfluorinated titanium phosphates synthesised to date. Other experiments are currently in progress.

Acknowledgement

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Note added at proof. Just after receiving the comments of the referees, a new mixed valence Ti^{III}–^{IV} phosphate, different from ours, was published.[31]

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