Synthesis and characterization of the new microporous fluorogallophosphate Mu-2 with a novel framework topology

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A new three-dimensional microporous fluorogallophosphate whose structure consists of a cubic arrangement of double-four-ring units (D4R) hosting F^- anions was synthesized from a fluoride-containing aqueous medium in the presence of 4-amino-2,2,6,6-tetramethylpiperidine as organic template.

Since 1985, a large number of gallophosphates with microporous frameworks obtained by hydrothermal synthesis have been reported in the literature.[1] The use of the fluoride method[2] led to the discovery of the large pore cloverite, a structure with a three-dimensional 20-membered-ring channel system,[3] the LTA-type $GaPO_4$[4] and several gallophosphates named ULM-*n*.[5] In fact, it was shown that the fluoride anions play a structural role stabilizing the double-four-ring (D4R) units of the structure.[3] This type of secondary building unit was also observed for the gallophosphate Mu-1,[6] which is constituted of isolated D4R units, and the fluorogallophosphate Mu-3[7] whose structure consists of chains of D4Rs. The specific location of F^- trapped within this type of unit was also previously observed for the gallophosphate ULM-5,[8] but in this case F^- is also a component of the framework as it bridges the gallium atoms. Here we report the synthesis and characterization of a new fluorogallophosphate, Mu-2, which was obtained in an aqueous fluoride-containing medium in the presence of 4-amino-2,2,6,6-tetramethylpiperidine as organic template. This organic species was previously introduced into an aluminosilicate gel and led to the crystallization of the precursor of ferrierite.[9] The chain-like fluorogallophosphate Mu-3 was obtained in a quasi-non-aqueous medium in the presence of the same organic template.[7]

Mu-2 was synthesized from an aqueous fluoride-containing mixture in the presence of 4-amino-2,2,6,6-tetramethylpiperidine (R). Typically, the molar composition of the starting gel was $1Ga_2O_3 : 1P_2O_5 : 0.3HF : 1R : 80H_2O$. The gel was prepared by first mixing 0.56 g of the gallium source [an amorphous gallium oxide hydroxide obtained by heating a gallium nitrate solution (Rhône-Poulenc) at 250 °C for 24 h] with 0.58 g of phosphoric acid solution (85% H_3PO_4, Normapur, Prolabo) and the required amount of distilled water (3.4 g). After homogenization 0.04 g of hydrofluoric acid (40% Normapur, Prolabo) and 0.39 g of 4-amino-2,2,6,6-tetramethylpiperidine (Fluka, purum $>97\%$) were added successively under stirring. The gel was mixed at room temperature for 1 h and transferred to a Teflon-lined stainless-steel autoclave. After heating at 170 °C for 5 days, the solid obtained was washed with distilled water. Mu-2 was easily isolated from the batch by ultrasonication in the form of large rounded truncated cubes with a size close to 100 μm (Fig. 1). This preparation also gives an unidentified phase (probably a layered material) which does not contain fluoride anions.

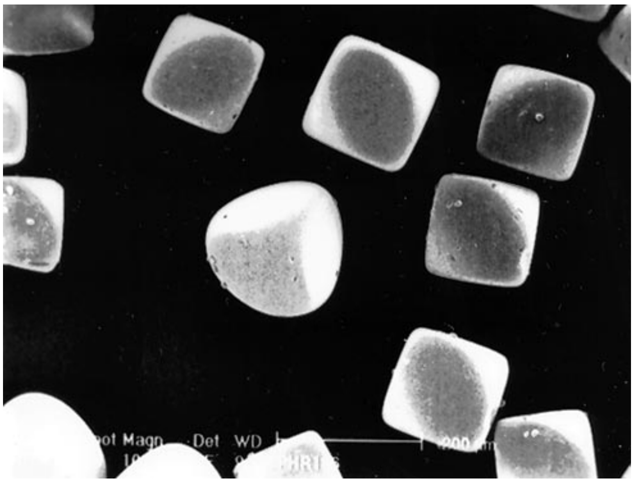

Fig. 1 Scanning electron micrograph of rounded truncated cubes of Mu-2

The X-ray diffraction pattern of Mu-2 was unambiguously indexed with a cubic *I*-centered cell with $a = 16.377(1)$ Å. The elemental analysis of the as-synthesized sample of Mu-2 gave the following composition (wt.%): Ga: 32.9; P: 13.6; F: 1.73; R: 14.4. This analysis is in good agreement with the electron microprobe analysis performed on the rounded truncated cubes. The amount of organic species was confirmed by quantitative ^1H liquid NMR spectroscopy (by dissolution of the sample in 6 M HCl) and 6 molecules were found per unit cell. From the ^{13}C CP-MAS solid-state NMR spectroscopy the amine is occluded in a protonated form (probably monoprotonated according to the structure determination).‡

The TG and DSC curves of as-synthesized Mu-2 were recorded under air on a Setaram TG/DSC111 thermoanalyser.

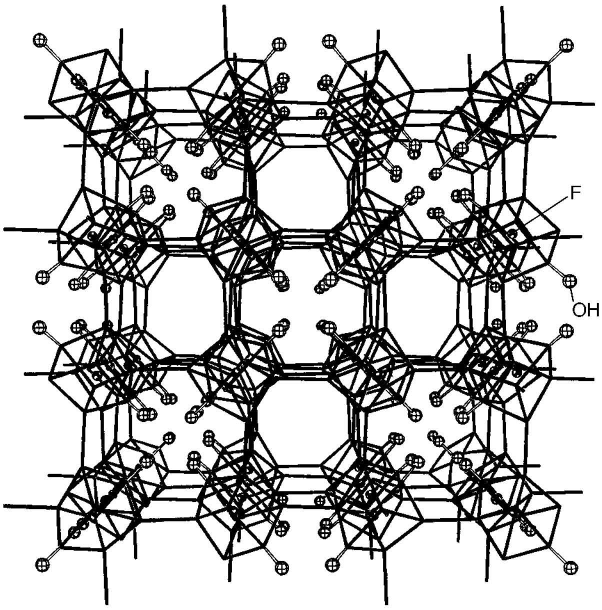

Fig. 2 Perspective view of the framework of the gallophosphate Mu-2 showing the two types of cage-like voids (one without OH group; the other with 8 T-OH groups); the Ga and P atoms are located at the vertices

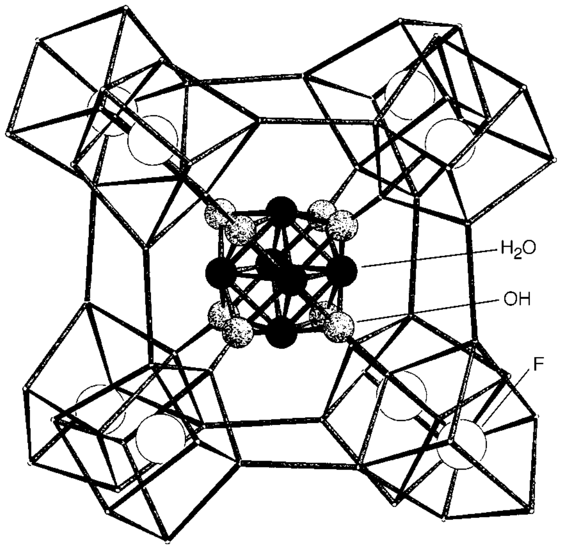

Fig. 3 The $(OH)_8(H_2O)_6$ cluster surrounded by eight D4Rs

Two broad endothermic peaks located at *ca*. 100 and 200 °C are observed. They correspond to the elimination of the physisorbed water molecules, the dehydroxylation of the T-OH groups and the removal of the fluoride anions (mass loss: 7.2%). The second mass loss (*ca*. 14.4%) corresponds to the removal of the organic species (several exothermic peaks on the DSC curve) and is achieved after calcination at 1000 °C. This new gallophosphate shows a low thermal stability. The structure collapses at *ca*. 300 °C and the cristobalite-type gallophosphate crystallizes at 600 °C.

The ^{19}F MAS solid-state NMR spectrum of Mu-2 displays a single signal at -72 ppm (relative to $CFCl_3$). Such a chemical shift value was previously found for the LTA- and CLO-type gallophosphates and is unambiguously assigned to fluoride anions trapped in the D4R units of the structure.

Taking into account all of the results and the density measurement (d_{mes} = 2.48 kg m^{-3}), the unit cell formula of Mu-2 is $Ga_{32}P_{32}O_{120}(OH)_{16}F_6(C_9H_{21}N_2)_6 \cdot 12H_2O$.

The structure analysis based on single crystal and powder X-ray data§ revealed that Mu-2 has a novel framework topology (Fig. 2). The gallophosphate framework of Mu-2 can be completely built from D4Rs as the fundamental building blocks. As observed from ^{19}F NMR spectroscopy, the D4Rs are occupied by a fluoride anion (according to the chemical analysis the occupancy factor is 0.75). Each $[Ga_4P_4O_{15}(OH)_2F]$ building block is interconnected with six other building blocks *via* common oxygen atoms. The remaining two corners of the D4R are T-OH groups (one P-OH and one Ga-OH). The interconnection of the D4Rs forms a three-dimensional but interrupted framework which has a three-dimensional pore system of 8MR pore openings. The framework which shows a strict alternation of phosphorus and gallium atoms at the T sites possesses two types of cage-like voids. The first type of cage (six per unit cell) does not contain any OH groups, whereas the second one (two per unit cell) displays 8 T-OH groups. The protonated 4-amino-2,2,6,6-tetramethylpiperidine occluded into the first type of cage (with a free volume of *ca*. 500 Å^3) is disordered.

An interesting feature of this structure is the $(OH)_8(H_2O)_6$ cluster (Fig. 3) present in the second type of cage. The sixteen T-OH groups of the D4Rs point either to the origin (0, 0, 0) or the center of the unit cell ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) such that the OH groups are arranged in two $(OH)_8$ cubes [the O–O distance between neighboring hydroxyl groups is 2.85(1) Å]. The six water molecules which are located close to the middle of the cube faces form hydrogen bridges to each other and the hydroxyl groups. The center of the $(OH)_8(H_2O)_6$ cluster, however, is vacant.

Notes and References

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‡ For the structure determination 2885 intensities from a twinned single crystal were collected on a four circle Syntex R3 diffractometer in omega scan mode. 1014 reflections remained after merging and were used for the structure analysis based on the SHELXTL program system.[10] The structure was solved by direct methods.

§ The XRD powder data were recorded on a Siemens D5000 diffractometer with a linear 6° position sensitive detector in Debye–Scherrer geometry (Ge monochromator, λ = 1.5406 Å). The Rietveld refinement (2θ range = 7–97°, space group $I23$, number of observations = 3790, number of reflections = 404, number of structural parameters = 40) performed with the XRS-82 program[11] converged to R_F = 0.077, R_{wp} = 0.107 while the statistically expected R_{exp} is 0.113. A detailed description of the structure including the atomic coordinates, displacement parameters, bond lengths and angle of Mu-2 will be published elsewhere.[12] CCDC 182/928.

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