A novel pyridine-templated open framework gallophosphate

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A new type of gallium phosphate open framework material has been prepared from solvothermal synthesis and its structure solved using microcrystal X-ray diffraction at a synchrotron source.

The rational design of open framework materials is an established goal of materials science.[1] The potential uses for rationally designed molecular sieves are many, but of particular interest are the applications of such materials as shape selective catalysts for fine chemical synthesis. Within this area the study of gallium phosphates has provided a wide range of interesting new open framework structures, including Cloverite,[2] which has the largest pore size of any microporous material. The work of Férey has illustrated particularly well the structural richness of the gallophosphate system.[3]

The most common methods of preparing open framework materials use templating and the cross-linking of layered materials. Templating involves the use of an organic molecule to organise the inorganic framework into an open structure, while cross-linked materials consist of layers that are joined together so as to produce voids and cavities in the interlayer region. This paper reports the synthesis of a new open framework gallium phosphate material which contains features of both of these types of structures; layers of open zeolite-like structure linked to form a completely novel type of open framework architecture with interconnecting eight membered ring channels. The new material is templated by pyridine.

In the course of a systematic study of the effects of various conditions on the product of a solvothermal gallium phosphate synthesis in which pyridine serves as both solvent and template, a novel type of open framework gallium phosphate structure has been prepared. The new material, pyridine-GaPO-1 [formula: $Ga_6(PO_4)_6F_2\cdot 2C_5H_6N\cdot H_2O$], was prepared by a solvothermal synthesis with pyridine (99%, Fischer) as the solvent and hydrofluoric acid (70% solution in pyridine) as a source of fluoride ions. Phosphoric acid (0.2 g, 85% weight aqueous solution, Aldrich) was diluted with a small amount (2 ml) of distilled water in a plastic beaker and to this pyridine (0.8 ml) was added with vigorous stirring. Ground gallium sulfate (0.5 g, 99.8%, Aldrich) was then added, followed by hydrofluoric acid (*ca.* 0.02 ml) giving an approximate molar oxide ratio of Ga_2O_3: P_2O_5: F: 8 pyridine: 8 H_2O. The mixture (pH 5) was stirred at room temperature for 20 min, transferred to a Teflon-lined stainless steel autoclave and heated at 180 °C for 72 h. The product, a crop of tiny colourless crystals, was recovered by suction filtration, washed with distilled water and acetone and dried at room temperature.

The crystal size (max. $20 \times 20 \times 8$ μm) proved too small for single crystal data collection on a conventional laboratory four circle diffractometer, so data were collected using a Bruker AXS SMART CCD area-detector at the high-flux microcrystal diffraction facility (station 9.8) of the SRS at Daresbury using a wavelength of 0.6849 Å.†

The structure can be thought of as consisting of two parts. The first is a zeolite-related layer made up of $Ga_2P_2O_8$ single four-rings (S4Rs). These S4Rs are linked together to form a layer that contains eight-ring windows. When viewed parallel to the $(11\bar{1})$ direction (Fig. 1), the structure closely resembles that of the zeolite ABW,[4] which is comprised of eight-rings linked by four-rings. This topology has also been observed for a number of other zeolites and zeolite analogues.[5] All of the gallium and phosphorus atoms in layered regions of the structure are tetrahedrally coordinated to four oxygen atoms, and the gallium and phosphorus atoms alternate. These zeolite-like layers are linked into a three-dimensional structure by cross-linking units consisting of a dimeric unit of octahedrally coordinated gallium atoms. The two gallium-centred polyhedra share the two fluorine atoms that make one edge of the octahedra to give a unit with the formula $Ga_2F_2O_8$. The overall structure consists of a three-dimensional framework with interconnecting eight-ring channels (Fig. 2) formed by the linking of the layers, producing pores that run parallel to the plane of the layers, and by the zeolitic nature of the layers themselves, which stack on top of each other to form channels perpendicular to the plane of the layers (Fig. 3). The $Ga_2F_2O_8$ unit causes half of the eight-ring channels to be distorted to an almost circular shape, while the others maintain the oval form normally observed in gallium phosphates. The dimeric $Ga_2F_2O_8$

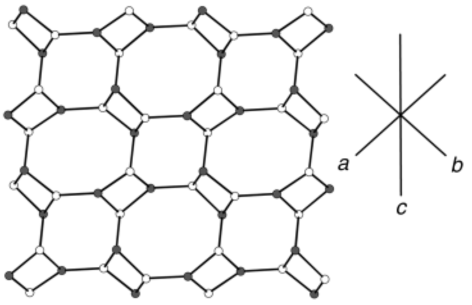

Fig. 1 A view of the zeolite-like layers parallel to the $(11\bar{1})$ direction illustrating the system of eight-rings connected by four-rings. The gallium and phosphorus atoms are shown as open and shaded spheres, respectively. The oxygen atoms would then be placed near the centres of the lines joining the Ga and P atoms.

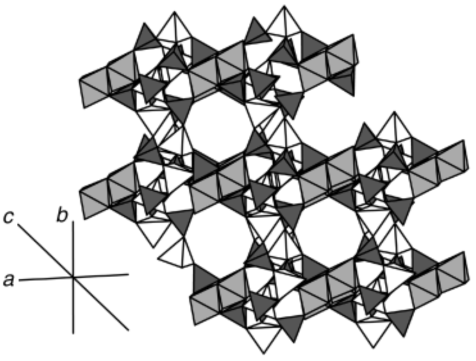

Fig. 2 Polyhedral view of the inorganic framework parallel to the $(11\bar{1})$ direction showing the linking of the layers by the $Ga_2F_2O_8$ dimer and the channels produced that run parallel to this direction. The layers run vertically up the diagram. Template molecules are not shown. The shaded and unshaded tetrahedra are PO_4 and GaO_4, respectively, and the $Ga_2F_2O_8$ unit is shown as lightly shaded edge sharing octahedra.

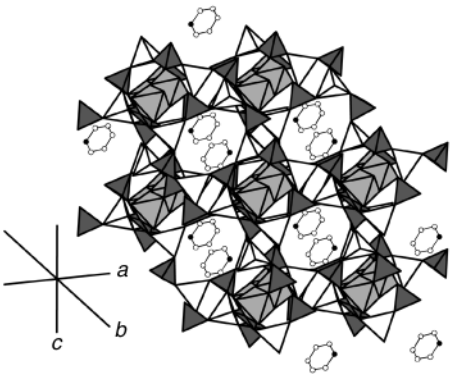

Fig. 3 Polyhedral view parallel to the $(11\bar{1})$ direction showing the eight-ring channels produced by the stacking of the zeolite layers. Also shown is the position of the pyridine template molecules inside these channels. The shaded and unshaded tetrahedra are PO_4 and GaO_4 respectively, and the $Ga_2F_2O_8$ unit is shown as lightly shaded edge sharing octahedra. The nitrogen atoms are shown as shaded spheres and the carbons as unshaded spheres.

unit found linking the layers has not been observed previously in this type of material but the linking of layers into a 3D structure is similar to that observed in the previously reported cyclam-GaPO material,[6] in which an octahedral gallium–cyclam complex joins layers of double four-ring units.

The pyridine template is protonated and hydrogen bonded to a solvent water molecule, which is disordered over two crystallographic sites. The strong binding of this water molecule is illustrated by thermogravimetric analysis, which shows a mass loss corresponding to the loss of water at around 250 °C (observed 1.2%; calculated 1.5%). A second mass loss corresponding to loss of pyridine occurs between 330 and 360 °C (observed 13.0%; calculated 13.3%). The material loses crystallinity at this temperature.

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Notes and references

† *Crystal data* for $Ga_6(PO_4)_6F_2{\cdot}2C_5H_6N{\cdot}H_2O$: M = 1204.38, triclinic, space group $P\bar{1}$ (no. 2), a = 11.391(4), b = 12.414(3), c = 12.846(4) Å, α = 71.04(3), β = 68.39(2), γ = 66.88(2)°, U = 1518.3(8) Å^3, T = 150 K, D_c = 2.630 g cm^{-3}, Z = 2, μ(Mo-Kα) = 5.682 mm^{-1}, 7704 reflections measured, 7319 observed (R_{int} = 0.029) which were used in all calculations. The final $wR(F^2_{\text{all data}})$ was 0.1288 and $R(F_{\text{all data}})$ was 0.0481. The crystal structure was solved using direct methods and refined by full-matrix least squares on F^2. Corrections were made for synchrotron beam intensity decay as part of the standard inter-frame scaling procedures.

CCDC 182/1407. See http://www.rsc.org/suppdata/cc/1999/2037/ for crystallographic files in .cif format.

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