The Synthesis and Crystal Structure of a Novel Oxyfluorinated Microporous Gallium Phosphate Using Diaminobutane as a Template

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The synthesis and crystal structure of a novel open framework gallium fluorophosphate is described; the structural units contain 5 and 6-coordinated Ga atoms bridged by F and PO_4 groups to form asymmetric ten-membered rings that house the diaminobutane template molecules, and which are connected to give rise to bell-shaped channels along [010] of approximate dimensions 7 × 9 Å.

The last decade has seen the discovery of many novel aluminophosphates and gallophosphates with open framework structures.[1–4] Many of the aluminophosphates bear a close, if not exact, resemblance to corresponding aluminosilicate zeolites. The substitution of aluminum by gallium in these structures and/or the use of HF as a mineralizing agent, however, has lead to the hydrothermal synthesis of some unique microporous structures.[5–7] This is partly due to the propensity of gallium to adopt a more variable and expanded coordination environment compared to aluminum. Here, we report the synthesis and crystal structure[†] of a novel oxyfluorinated gallium phosphate, $Ga_3(PO_4)_3F_2P{\cdot}C_4H_{14}N_2$.

This compound was synthesized under hydrothermal conditons using diaminobutane as the templating agent, and GaF_3 as the fluoride ion source. Cab–O–Sil was added to the initial reaction mixture, though no silicon was detected in the crystalline product. Typically the reaction mixture, of molar composition $1.0Ga_2O_3$: $2.0P_2O_5$: $1.25SiO_2$: $1.50NH_2(CH_2)_4NH_2$: $120H_2O$, was stirred to homogeneity, sealed in a Teflon-lined stainless autoclave and heated at 150 °C for 3 days under autogenous pressure. The resulting product, consisting of large single crystals and some amorphous material was filtered, washed with water and dried in air at ambient temperature.

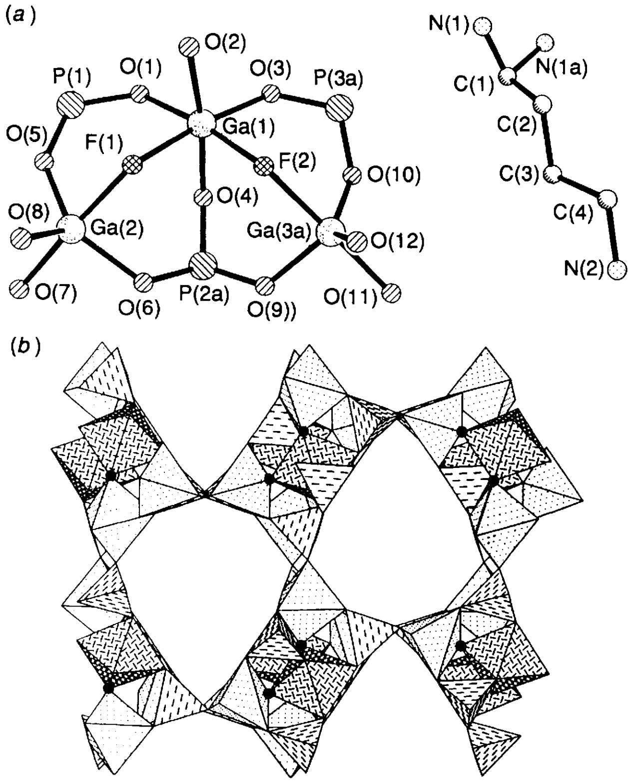

Fig. 1 (*a*) The asymmetric unit of the gallofluorophosphate structure. Selected and average bond lengths (Å): P–O 1.53, Ga(1)–O 1.92, Ga(2,3)–O 1.86, Ga(1)–F 1.97, Ga(2,3)–F 2.02.
(*b*) Polyhedral drawing of a sheet onto the (010) plane, showing the interconnection of the gallium octahedra (cross-hatched), the five-coordinate gallium polyhedra (dotted) and the phosphorus tetrahedra (dashed lines).

A suitable crystal for X-ray analysis[†] was obtained from the synthesized material. The asymmetric unit [Fig. 1(*a*)] contains three crystallographically inequivalent PO_4 tetrahedra that share an oxygen with four adjacent gallium atoms. Of the three inequivalent gallium atoms, one is octahedrally coordinated by four oxygen atoms and two fluorine atoms (GaO_4F_2). This gallium atom is directly connected to two gallium atoms located at the centres of distorted trigonal bipyramids (GaO_4F) *via* vertex-bridged fluorine atoms, and to the pentacoordinate and octahedral gallium atoms through the vertex-shared phosphate groups. These structural features are unique so far in gallium oxyfluorophosphates, although similar fluorine bridging is observed in related compounds. The $AlPO_4$–CJ2 structure, for example, is also characterized by aluminum coordination polyhedra sharing fluorine (or hydroxy) at the vertex,[6] and the dimeric gallium octahedral groups in $Ga_3(PO_4)(HPO_4)_2F_3(OH){\cdot}C_6N_2H_{14}{\cdot}0.5H_2O$ were found to share two fluorine atoms on a common edge.[7]

The three-dimensional framework is built up of two-dimensional nets composed of three and ten-membered rings. The estimated size of the marquise-shaped ten-membered ring which houses the diaminobutane template molecule is 7 × 9 Å. A polyhedral representation of these rings is shown in [Fig. 1(*b*)]. The two-dimensional nets are stacked to form channels along [010] (Fig. 2). The ten-membered rings show a strict alternation of gallium and phosphorus atoms, while the three-membered rings show Ga*–Ga§–P alternation, where Ga* corresponds to the gallium octahedra linked by a fluorine

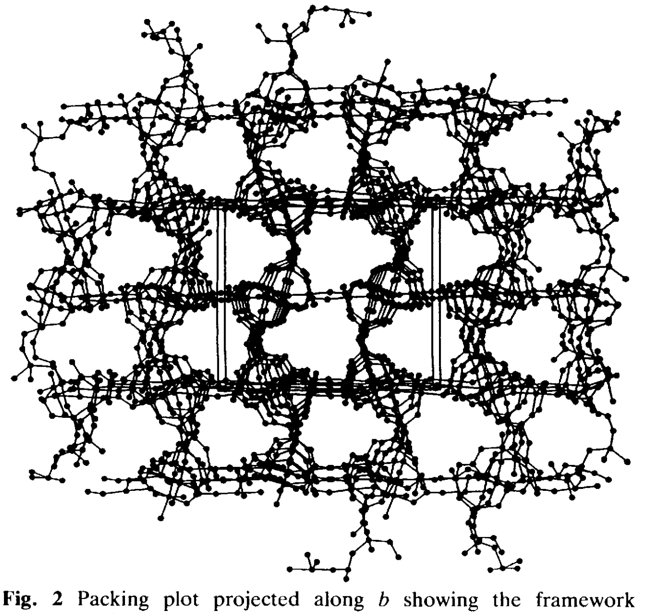

Fig. 2 Packing plot projected along *b* showing the framework structure, with Ga, O and P atoms all indicated by small filled circles. The amine template molecules are omitted for clarity.

corner and Ga§ to the distorted trigonal bipyramidal gallium linked by an oxygen atom. Furthermore, in the [001] and [100] planes, there are four-membered rings formed by Ga–P–Ga–P alternation.

The templates are trapped in the ten-membered rings with both amine head groups connected to the framework by hydrogen bonds. The N–H···O or N–H···F contact lengths are in the range 2.84–3.10 Å. The N atoms on one end of the template, however, are disordered and split with an occupancy of 0.6/0.4. This gives rise to uncertainty of the H atom positions attached to those disordered atoms.

We found average interatomic distances of 1.99 Å for Ga–F, 1.92 Å for octahedrally coordinated Ga–O in GaF_2O_4, 1.86 Å for pentacoordinate Ga–O in $GaFO_4$, and 1.53 Å for the P–O bond lengths, respectively. These values are similar to those found in $Ga_3(PO_4)(HPO_4)2F_3(OH){\cdot}C_6N_2H_{14}{\cdot}0.5H_2O$ which is the closest analogue to the title compound.[7] The rather large Ga–F distance (compared with the average distance of 1.90 Å encountered in gallium fluorides[8]) corresponds to the presence of N–H···F hydrogen bonds, which leads to an increase in the Ga–F bond length. In addition, one of the oxygen atoms on each of the five-coordinate gallium sites [O(7) and O(11); Fig. 1] are also hydrogen bonded with N atoms, which results in a larger Ga–O distance of 1.93 Å, compared with 1.84 Å for the other three Ga–O bonds.

Thermogravimetric–differential thermal analysis showed that no significant weight loss occurs until 420 °C. At this temperature, the material loses about 10% of its mass, a loss accompanied by an endothermic transition corresponding to the removal of the organic template from the pores. This is followed by a gradual weight loss and a very broad exothermic transition centred at about 510 °C associated with decomposition of the framework structure. The thermal stability of the title compound is quite high compared with other gallium phosphates such as $(NH_4)_{0.93}(H_3O)_{0.07}GaPO_4(OH)_{0.5}F_{0.5}$, which has a similar three-dimensional tunnel structure containing eight-membered rings,[7] and a decomposition temperature of 200 °C. The higher thermal stability may come from the strong hydrogen bonds of the template to the framework.

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† *Crystal data* for $Ga_3P_3F_2O_{12}(C_4H_{14}N_2)$: orthorhombic, space group *Pbca*, a = 10.063(2), b = 16.023(5), c = 18.486(3) Å, V = 2980.67 Å^3, M_r = 608.1, μ(Mo-Kα) = 5.80 mm^{-1}, D_c = 2.733 g cm^{-3}, crystal dimensions 0.18 × 0.08 × 0.02 mm. Data were collected on a Siemens P4 diffractometer equipped with a rotating anode, using Mo-Kα radiation. The scanning range was 3 to 60° 2θ, and the ω-2θ scan technique was used. The total number of reflections measured was 4724 for which 3845 were unique and 2060 were considered to be observed with $|F| > 6.0\sigma(|F|)$. The data were corrected for Lorentz polarisation and absorption effects. The structure was solved in the SHELXTL IRIS system by direct methods: the gallium and phosphorus atoms were first located and all of the remaining non-hydrogen atoms were located easily in the difference Fourier map. Refinement (245 variables) was by full-matrix least-squares analysis with anisotropic thermal parameters for all non-hydrogen atoms. The final Fourier residue of 1.4 eÅ^{-3} was located around the heavy Ga atoms (less than 1 Å away). The reliability factors converged to R_w = 0.0482, R = 0.0477. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ *Note added in proof*: After submission of this paper, we became aware of recent work by G. Ferey *et al.* on a triad of oxyfluorinated gallium phosphates whose lattice is isostructural with that reported here; the first of the series will appear in *J. Solid State Chem.*

References

1 S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan and E. M. Flanigen, *J. Am. Chem. Soc.*, 1982, **102**, 1146.

2 M. E. Davis, C. Saldarriaga, C. Montes, J. Garces and C. Crowder, *Nature*, 1988, **331**, 698.

3 J. B. Parise, *J. Chem. Soc., Chem. Commun.*, 1985, 606.

4 W. Tieli, Y. Guangdi, F. Shouhua, S. Changjiang and R. Xu, *J. Chem. Soc., Chem. Commun.*, 1989, 948.

5 M. Estermann, L. F. McCusker, C. Baerlocher, A. Merrouche and H. Kessler, *Nature*, 1991, **352**, 320.

6 G. J. Ferey, T. Loiseau, P. L. Lacorre and F. Taulelle, *J. Solid State Chem.*, 1993, **105**, 179.

7 T. Loiseau and G. J. Ferey, *J. Chem. Soc., Chem. Commun.*, 1992, 1197.

8 R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.