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ChemComm
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Two chain gallium fluorodiphosphates: synthesis, structure solution, and their transient presence during the hydrothermal crystallisation of a microporous gallium fluorophosphate†

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Received (in Cambridge, UK) 1st February 2002, Accepted 7th March 2002
First published as an Advance Article on the web 18th March 2002

Two novel gallium fluorodiphosphates have been isolated and their structures solved *ab initio* from powder X-ray diffraction data; the materials readily interconvert under hydrothermal conditions, and are metastable with respect to an open-framework zeolitic gallium fluorophosphate, during the synthesis of which they are present as transient intermediates.

The elucidation of the crystallisation mechanisms of microporous inorganic solids is currently the focus of considerable attention due to the uses of the materials in commercially important applications such as ion-exchange, gas separation and shape-selective catalysis. It is hoped that understanding how the complex architectures of open-framework inorganic solids are assembled will enable the synthesis of new microporous materials with properties tailored for a specific application; for example a solid with pore dimensions and polarity required by a specific sorption problem could be prepared by choice of reaction conditions prescribed by a mechanistic knowledge of the formation pathway. Aside from the well-known microporous aluminium silicate zeolites that find widespread industrial use, most recent mechanistic studies have focussed on the formation of open-framework phosphates.[1–4] Time-resolved studies performed *in situ* during the hydrothermal reactions used in the production of these microporous solids have provided some of the most striking data concerning reaction mechanism: for example, accurate crystallisation curves are obtained by time-resolved diffraction[5] and *in situ* NMR has revealed the solution presence of prenucleation building units.[4,6]

During *in situ* diffraction studies of the formation of three-dimensional, open-framework gallium fluorophosphates, we have reported the presence of transient crystalline intermediate phases that appear prior to the onset of the expected product.[7–9] Although we have subsequently isolated novel metastable phases from the same reaction mixtures employed in these studies,[10–13] until now we have never stabilised any of the intermediate phases. Herein we describe the synthesis of two new gallium fluorodiphosphates; the solids present rare examples of materials synthesised hydrothermally that include the diphosphate group, have novel structures and are seen as transient intermediates during the formation of a microporous gallium fluorophosphate, ULM-3.[9]

One of the two new solids, $Ga(P_2O_7)F{\cdot}H_3N(CH_2)_3NH_3{\cdot}3H_2O$ (**1**) was isolated as a pure, polycrystalline powder from a reaction mixture of composition 0.5 $Ga(NO_3)_3{\cdot}xH_2O$: 3 P_2O_5 : 5.4 DAP : 6.0 HF : 208 H_2O (DAP = 1,3-diaminopropane) that was held at 90 °C in a Telfon-lined autoclave for 1 week. Higher reaction temperatures resulted in the formation of microporous ULM-3, and the use of H_3PO_4 instead of P_2O_5 resulted in the formation of an already characterised gallium fluorophosphate.[10] The second new phase, $Ga(P_2O_7)F{\cdot}H_3N(CH_2)_3NH_3{\cdot}H_2O$ (**2**) was prepared under identical conditions, except for the use of a 50 : 50 ethylene glycol–water mixture as solvent and again a polycrystalline powder was formed. The structures of the two new materials were solved *ab initio* from laboratory powder X-ray diffraction data.‡

Both (**1**) and (**2**) contain the same inorganic component to their structure: a one-dimensional chain constructed from octahedral $\{GaO_4F_2\}$ units linked *via* axial fluorine ligands, and shared ditetrahedral $\{P_2O_7\}$ units, Fig. 1.

All bond lengths agree very well with those previously seen in the now large family of gallium fluorophosphates[14] and the geometry of the $\{P_2O_7\}$ unit is the same as observed in other diphosphates.[15,16] The inorganic chains have an overall negative charge and this is balanced by 1,3-propylenediammonium cations, which are also hydrogen bonded to the oxygen and fluorine atoms of the chains and occluded water molecules. The

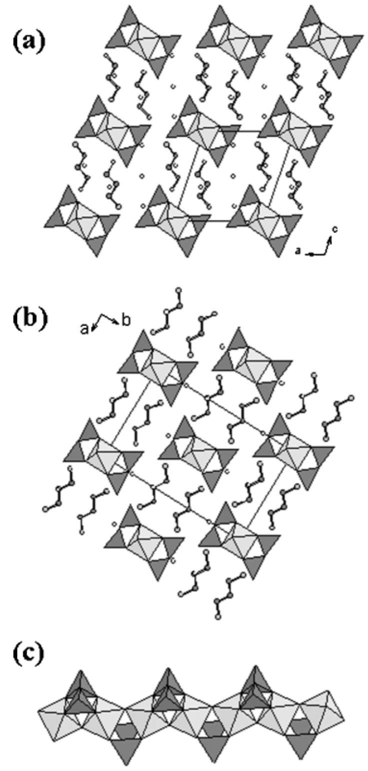

Fig. 1 (a) A view of (**1**) along the chain axis, (b) A view of (**2**) along the chain axis, and (c) part of the infinite chains found in both (**1**) and (**2**). Pale grey polyhedra are gallium centred and dark grey are phosphorus centred; small dark circles are carbon atoms, pale circles nitrogens and open circles, oxygens.

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† Electronic supplementary information (ESI) available: crystal data, atomic coordinates and metrical data for **1** and **2**. See http://www.rsc.org/suppdata/cc/b2/b201178f/

DOI: 10.1039/b201178f

isolation of diphosphates under mild hydrothermal conditions is unusual; among the hundreds of phosphates previously reported to be prepared by the hydrothermal method, virtually all contain isolated {PO_4} units that are bridged by metal containing polyhedra. To the best of our knowledge only three such materials have been reported: phosphate–diphosphates of gallium and vanadium,[15] and a nickel fluorodiphosphate.[16] This is perhaps not surprising since the hydrothermal synthesis conditions usually employed involved low pH under which the $P_2O_7^{4-}$ ion is readily hydrolysed to PO_4^{3-}. Our work demonstrates that by use of mild hydrothermal conditions (<100 °C rather than the usual 150-200 °C) and P_2O_5 instead of H_3PO_4 it is possible to isolate diphosphate-containing solids.

The two phases we describe have been observed previously *in situ* during time-resolved diffraction studies of the synthesis a three-dimensional, open-framework gallium fluorophosphate, notably only when P_2O_5 was used as a reagent.[9] Fig. 2 shows time-resolved EDXRD data measured from within the hydrothermal reaction cell at the Daresbury synchrotron radiation source (Station 16.4) when (**1**) was heated in water at 150 °C. With the use of a three-element solid-state detector, we are now able to measure a large extent of diffraction data, and can assign every peak of a transient intermediate phase as arising from (**2**). In our previous attempts to isolate the intermediate phase (during ULM-3 formation) from the *in situ* reaction cell by quenching to room temperature, we observed that conversion to a second, the unidentified, crystalline phase took place.[9] We can now identify this as (**1**), the trihydrate of the gallium fluorodiphosphate. On returning the cell to the *in situ* cell, and continuing heating, we observed the crystallisation pathway shown in the Fig. 2.

The chain phases we describe are clearly metastable, and we postulate they must form by partial hydrolysis of the P_2O_5 starting material, a process that releases $P_2O_7^{4-}$ anions into solution or at least retains some of P–O–P linkages as P–O–Ga bonding is developed. Our successful stabilisation of phases that incorporate diphosphate units indicates that the use of P_2O_5 as a reagent for the mild hydrothermal synthesis of phosphates is worthy of a detailed examination, with the goal of producing new three-dimensional, open-framework structures. The ease of interconversion of (**1**) and (**2**) and their dissolution followed by crystallisation of an open-framework material suggests that similar processes might be taking place in solution during the formation of other microporous fluorophosphates. The assembly of low-dimensional metastable phases prior to the formation of a thermodynamically stable open-framework is a possible pathway for crystallisation,[2,3] and our results provide direct (*in situ*) experimental data that substantiates the model as a plausible reaction mechanism for the formation of open-framework phosphates. It is noteworthy that Rao and coworkers have reported the transformation of chain zinc phosphates into 2D and 3D structures, and so it appears that the building up of 3D architectures from lower-dimensional structures is a common route for the crystallisation of phosphates.[3,19,20]

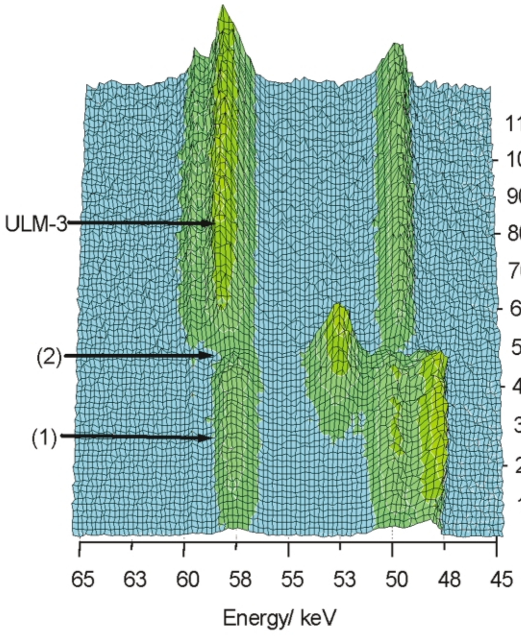

Fig. 2 *In situ* EDXRD data measured within the hydrothermal autoclave during the heating of (**1**) under hydrothermal conditions at 150 °C.

Notes and references

‡ Powder X-ray diffraction data were measured on a Siemens D5000 diffractometer using Cu-Kα radiation ($\lambda = 1.5418$ Å). Pattern indexing was performed by means of the program DICVOL91[17] from the first twenty lines. Structure determinations were performed using the EXPO package, which combines a full pattern decomposition program EXTRA and a direct method program SIR97 optimized for powder diffraction data.[18] *Crystal data* for **1**: monoclinic, space group $P2_1/m$ with $a = 9.5724(9)$, $b = 7.1632(6)$, $c = 9.9780(9)$ Å, $\beta = 108.816(5)°$ and $Z = 2$. *Crystal data* for **2**: orthorhombic, space group *Cmcm* with $a = 10.3093(4)$, $b = 15.9456(6)$, $c = 7.2219(3)$ Å and $Z = 4$.

CCDC reference numbers 179010 and 179011.

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