

**Experiment title:**

High resolution powder diffraction of microporous materials

Experiment number:
CH-261**Beamline:**

BM16

Date of experiment:

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Shifts:

12

Local contact(s):

Gavin VAUGHAN

*Received at ESRF:***1 SEP. 1997****Names and affiliations of applicants** (* indicates experimentalists):Russell MORRIS*, Philip LIGHFOOT*, Graham NOBLE*, Paul WRIGHT
University of St. Andrews, School of Chemistry, St. Andrews, Scotland**Report:**

Powder Diffraction of STA-2

Data were collected on powder samples of the new aluminophosphate STA-2, prepared via conventional alkali cation-free AlPO hydrothermal syntheses with the compositions AlPO_4 , $\text{MgO} \cdot 1\text{Al}_0.9\text{PO}_4$, $\text{Co} \cdot 1\text{Al}_0.9\text{PO}_4$ and $\text{Si}_{0.1}\text{AlP}_{0.9}\text{O}_4$. Although they clearly have similar structures the framework substitutions do produce changes in the unit cell dimensions and in the diffractograms. In a parallel experiment, a single MgAPO microcrystal prepared in the presence of Na^+ was studied on beamline ID- 11, BL2 and the solid became the second such material to have its structure solved in this way. Figure 1 shows a single cage of the solid, containing a closely fitting template molecule. The solid has a three-dimensionally connected small pore structure.

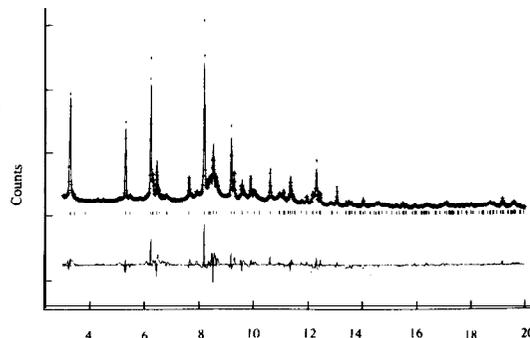
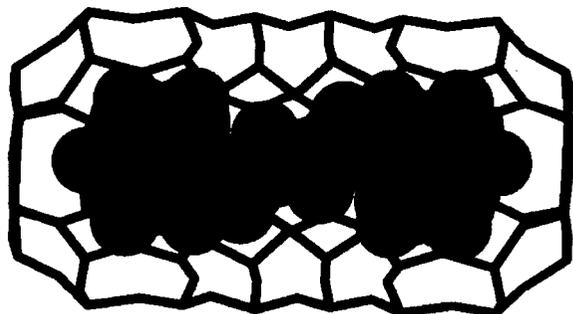


Figure 1. The experimentally-determined position of the template within the large cavities in STA-2, with the template represented by a space filling model and the inorganic framework represented by a line drawing (left) and Fitted experimental X-ray powder diffraction profile collected at station BM16, at the ESRF (right).

To prove that the structure determined from the single crystal diffraction at 200K is essentially the same as that the powder samples of STA-2 prepared without alkali cations the powder diffraction data collected at the ESRF the MgAPO-STA- 1 were matched using the structural parameters determined by microcrystal diffraction, allow the unit cell parameters and instrumental parameters (peak half-width, zero-point) to vary. The fit (figure 1, R= 11.4%, $R_p = 8.4\%$, with unit cell parameters at room temperature of $a=13.0121(7)\text{\AA}$ and $c=30.406(2)\text{\AA}$) is sufficiently close to confirm it is the same phase, although further refinement is required to take into account the effects of stacking faults and of additional thermal motion. Further studies are in progress to determine the nature of the structural distortions caused by the framework substitution.

Ab Initio Structure solution of gallium methylphosphonates

High resolution powder X-ray diffraction data were collected on two gallium aluminomethyl phosphonates. The pattern was indexed using the program TREOR90 to give an orthorhombic cell, with systematic absences consistent with spacegroup Pbcm. A Le Bail structure factor extraction was performed and 730 reflections in the range $5^\circ < 2\theta < 30^\circ$ were input into the direct methods program SIRPOW91. From the direct methods the gallium and phosphorus atoms were identified. The oxygen and carbon atoms were then located by difference Fourier techniques. The final cycle of least squares refinement yielded a unit cell of $a = 7.0716(1)\text{\AA}$ $b = 15.6755(3)\text{\AA}$ $c = 15.2580(3)\text{\AA}$, $R_p=0.13$, $R_{wp}=0.19$, and $R_F=0.17$. The final refined fit shows some residual problems with the peak shape due to anisotropic peak broadening. This can be partially fitted using the hkl-dependent broadening function in the GSAS suite of programs using the 110 plane although the work to complete the refinement satisfactorily is still in progress. Notwithstanding this the structure of the material can be described in terms of chains of gallium-centered octahedra running parallel to the 100 direction. Each GaO_6 shares one oxygen atom (ie a corner) with its neighbouring octahedra. The PO_3CH_3 tetrahedra then bridge two of these octahedra in the same chain via the sharing of two of the oxygens, leaving the chains to be held together by hydrogen bonding involving the last of the three oxygens on the tetrahedron. The motif present in this material is fairly common in the chemistry of aluminium phosphates, with a number of materials, both natural such as the mineral tancoite, and synthetic having related structures. The layered aluminium methylphosphonate solved in this department also has a related arrangement.

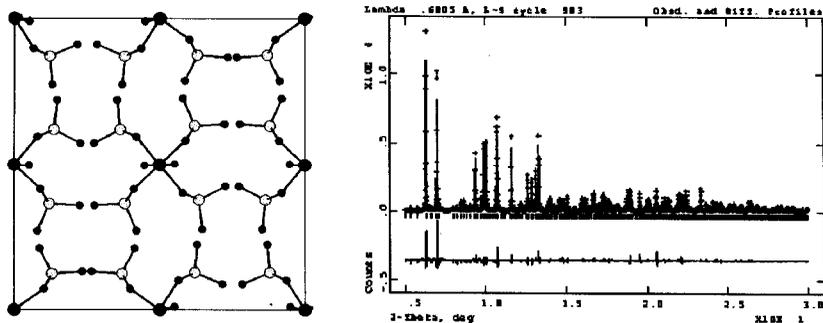


Figure 2. The structure of structure of gallium methylphosphonate viewed parallel to the 100 direction (left) and the final observed, calculated and difference plots for the Rietveld refinement against BM16 data.