



	Experiment title: Structural determination of aluminophosphate and gallophosphate compounds from powder diffraction: development of a new direct space resolution approach	Experiment number: CH-1533
Beamline: BM01B	Date of experiment: from: 2 February 2004 to: 3 February 2004	Date of report: 15/09/2005
Shifts: 3	Local contact(s): Wouter van Beek	<i>Received at ESRF:</i>
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Report:

Over the past decades, there has been a tremendous extension of the chemical and architectural diversity of open framework inorganic structures [A. K. Cheetham, G. F rey, T. Loiseau, *Angew. Chem. Int. Ed.* 1999, 38, 3268]. Following the developments of synthetic aluminosilicate zeolites and the discovery of their aluminophosphate analogues, there is a strong incentive for searching new architectures driven by their potential applications in catalysis or gas adsorption. In this context, one of our last results concerns the hydrothermal synthesis of two new aluminophosphates which present new architectures as revealed by their X-ray powder diffraction patterns. Patterns were indexed with the program DICVOL04 [A. Boultif & D. Lou r, *J. Appl. Crystallogr.*, 2004, 37, 724]. For compound **(1)** a quadratic solution ($a = 15.855(4) \text{ \AA}$, $c = 22.71(1) \text{ \AA}$ $V=5709(4) \text{ \AA}^3$; S.G.: $P 4_2/m b c$ or $P 4_2 b c$) was found with satisfactory figures of merit: $M_{20} = 26$ and $F_{20} = 70$ (0.007, 42). For compound **(2)**, splitting of some lines was observed and the symmetry was orthorhombic ($a = 15.934(5) \text{ \AA}$, $b = 16.003(4) \text{ \AA}$, $c = 24.260(5) \text{ \AA}$ $V= 6186(5) \text{ \AA}^3$; most probable S.G.: $P b c n$) with $M_{20} = 22$ and $F_{20} = 54$ (0.005, 73).

We have undertaken a new direct space resolution approach for finding structural models from powder data, in combination with NMR data for extracting connectivity information, and simulations for generating candidate structures [C. Mellot-Draznieks, S. Girard, G. F rey, J. C. Sch n, Z. Cancarevic & M. Jansen, *Chem. Eur. J.* 2002, 8, 4102]. The method, while being promising as shown by the case study of chiolite [J. Dutour, N. Guillou, C. Huguenard, F. Taulelle, C. Mellot-Draznieks & G. F rey, *Solid State Sciences*, 2004, 6, 1059], required high resolution synchrotron data as a consequence of high symmetries and important cell volumes. High resolution synchrotron powder data of these two aluminophosphates were then collected on the diffractometer of BM01B line of ESRF. Measurements were made with a Debye-Scherrer diffractometer geometry and a Si 111 analyzer crystal to select a monochromatic wavelength of 0.79986 \AA . The very fine powder was introduced in capillaries ($\phi = 1\text{ mm}$) and patterns were scanned in the range $1-55^\circ$ (2θ).

Compound **(1)**: The lack of contrast between aluminium and phosphorous atoms, the number of heavy atoms to find (12 in the non centric space group) and the exact overlapping of non equivalent reflections did not allow us to obtain

an exploitable starting solution by direct methods. Nevertheless, a value $|E^2 - 1|$ of 0.732 confirmed the assumption of a non centric space group as supposed from NMR spectra. Attempts to solve the structure by direct space strategy were undertaken by using FOX in the $P4_2bc$ space group, choosing the parallel tempering algorithm. First, fourteen independent fragments (7 PO_4 tetrahedra, 2 organic DAE molecules and 5 Al atoms) were considered, using random starting positions, however the computational search did not converge towards a reliable solution. Then we made the hypothesis that at least, one phosphate should be connected to four alumina (see Fig. 1) and the strategy was to use this “secondary building unit”, six PO_4 , one aluminium atom and two organic moieties, put randomly in the unit cell at the starting stage. The calculations converged in almost 48 hours to a layered framework where only two alumina of the PO_4Al_4 unit should be moved to increase their connectivity towards phosphate groups. The corresponding atomic coordinates were used as the starting model in the Rietveld refinement, which converged to $R_{wp} = 0.199$, confirming the validity of the hypothesis. Fourier difference calculations (SHELXTL) allowed then the location of the free water molecules. The final Rietveld refinement carried out in the angular ranges $3\text{-}55^\circ(2\theta)$ used 2371 reflections and involved 152 atomic coordinates. It corresponds to satisfactory crystal structure model indicators ($R_B = 0.055$) and profile factors ($R_p = 0.062$). Figure 2 shows the final fit obtained between calculated and observed patterns.

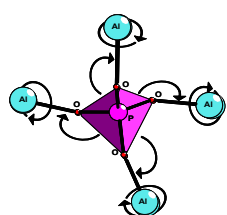


Fig. 1: Secondary building unit used in FOX

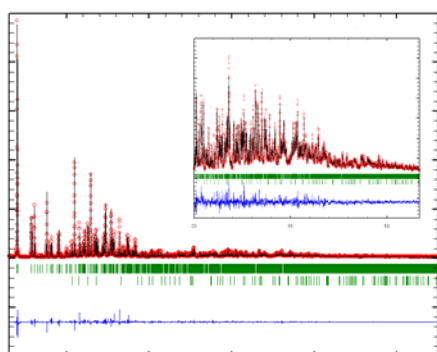


Fig. 2: Final Rietveld plot of (1)

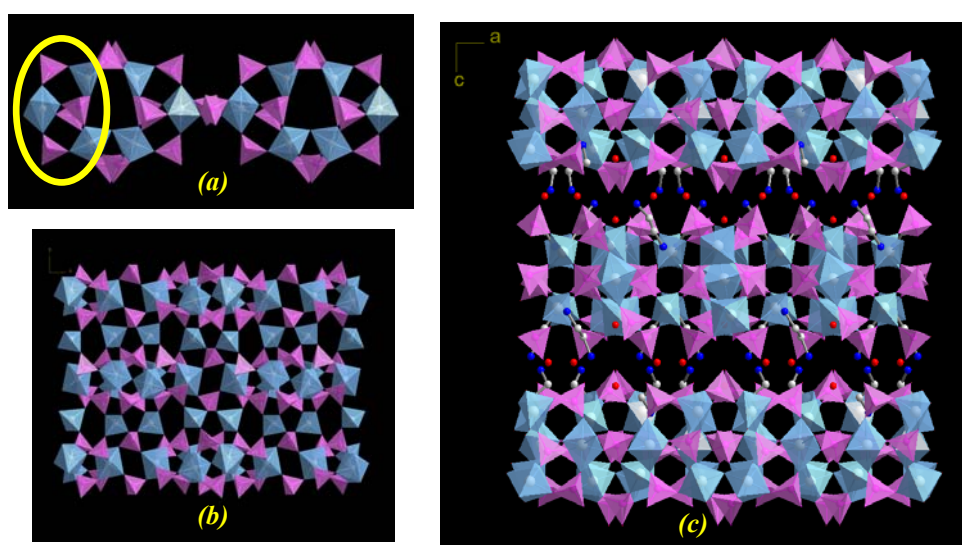


Fig. 3: (a) View of the connection of heptamers (yellow circle) for generating chain; (b) connection of three chains to form a layer; (c) projection of the structure of (1) along b .

The crystal structure of (1) can be described from $[\text{Al}_{10}(\text{PO}_4)_9(\text{PO}_3\text{OH})_5(\text{OH})]^{8-}$ layers perpendicular to the c axis. Aluminum atoms adopt the three possible coordinations: tetrahedra, trigonal bipyramid and octahedra. Three of the seven independent phosphate groups are connected to four alumina whereas the four others possess terminal oxygen or terminal hydroxyl pointing to the interlayer space. The triple layer can be described from heptamers Al_3P_4 (Fig. 3a) connected two by two directly via the hydroxyl and via four phosphate groups for generating 7 membered rings. These dimmers of heptamers are then connected via two phosphates to form chains running along a or b (Fig. 3a). The connectivity of the chains to form layers is insured by AlO_4 , generating 8 and 6 membered rings (Fig. 3b). The cohesion of successive layers is insured directly by strong hydrogen bonds between phosphates. The two amines and the water molecules reinforce the threedimensionality of the structure (Fig. 3c).

Compound (2): NMR calculations allowed us to determine the number of Al and P sites in the orthorhombic unit cell, in agreement with the $Pbcn$ space group. Similarities of unit cells led us to suppose that the two structures were extremely correlated and positions of fragments of the inorganic layer of compound (1) were transposed in the $Pbcn$ space group and used in FOX as starting stage. Calculations converged in almost 48 hours. The main difference between the two structures concerns hydroxyl groups, not present in compound (2) (Fig. 4).

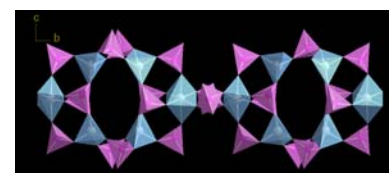


Fig. 4: View of the connection of for generating chain in (2).