	Experiment title: High resolution powder diffraction studies of zeolites and organozeolites	Experiment number: Ch1862
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Shifts: 6	Local contact(s): Prof. A. Fitch	
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Report: High resolution powder diffraction studies of zeolites and organic-inorganic hybrids were performed to answer specific structural questions and to solve novel structures.

1. Structural refinement of the novel gallosilicate zeolite TNU-7 and related phases
2. Data collection on zeolites and aluminophosphates for structure determination.
3. Data collection on organic-inorganic microporous hybrids

1. Structures of TNU-7 and related phases

The framework structures and extra-framework cation positions of the gallosilicates TNU-7, mazzite and mordenite have been refined against synchrotron x-ray diffraction data for the three materials (fig. 1).

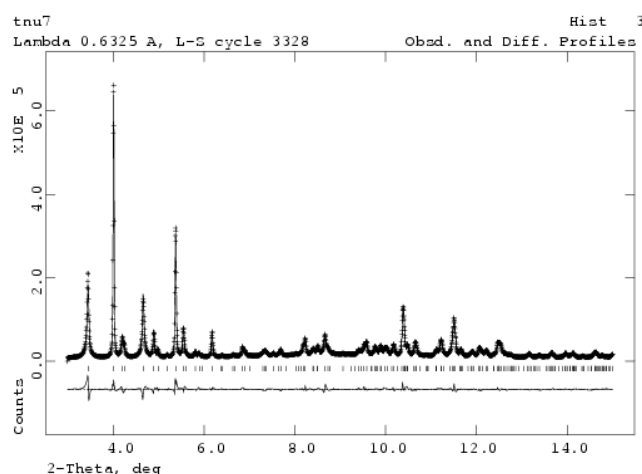


Fig. 1. Observed and fitted XRD profile of Na-TNU-7

The structure of TNU-7 is confirmed as a completely ordered intergrowth of gallosilicate mazzite and mordenite layers. Sequential formation of Na-Ga-mazzite, Na-TNU-7 and Na-Ga-mordenite with increasing Si/Ga ratio indicates a unique structure-directing role of Ga. While the positions of extra framework Na^+ cations in Na-TNU-7 show strong

similarities with those observed in the related phases, the positions of ion-exchanged cations Cs^+ , Sr^{2+} and La^{3+} are influenced strongly by the cationic radius. This is most apparent in the location of Cs^+ cations. Extra framework cation charge per T-site implies a higher charge associated with the MAZ region indicating chemical zoning within the structure results during synthesis. This work is to be reported at the 3rd International FEZA[1] conference and a more detailed report is in progress.

[1] S.J. Warrender, P.A. Wright, W. Zhou, P. Lightfoot, M.A. Camblor, C.-H. Shin, D.J. Kim and S. B. Hong *Proc. 3rd Int. FEZA conf.*, Prague, 2005

2. Novel zeolites and aluminophosphates

High resolution data was collected on the zeolites TNU-9, ZSM-25 and a new alumino-phosphate (TNU-12). ZSM-25 was identified as being isostructural with the natural zeolite paulingite, and efforts are currently being made, in combination with high resolution microscopy, to solve the other two structures, which have large, low symmetry unit cells. In addition, data was collected on a templated scandium phosphate[2], successfully confirming the partial structural model determined from single crystal diffraction from a very small crystal.

[2] S.R. Miller, A.M.Z. Slawin, P. Wormald, P.A. Wright *J. Solid State Chem.* 2005, 178, 1738-1752

3. Structure solution of porous organic-inorganic hybrids

Diffraction patterns were collected over repeated short time periods on aluminium phosphonates and a sodium scandium methylphosphonate. In particular, the scandium methylphosphonate gave a high quality diffraction pattern, albeit with some unreacted scandium oxide impurity (figure 2).

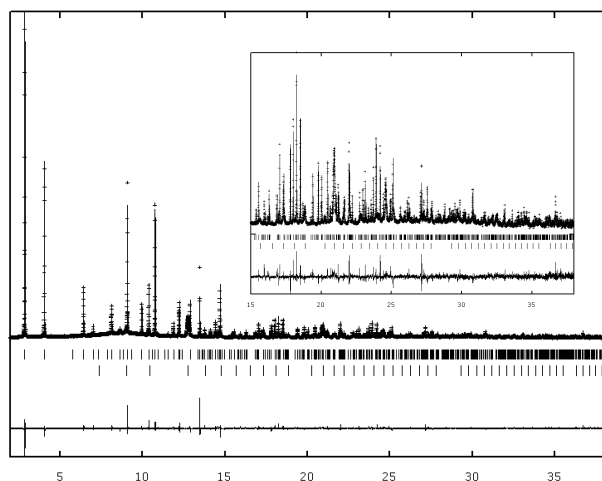


Figure 2. Measured and calculated diffraction pattern of $\text{NaSc}(\text{CH}_3\text{PO}_3)_2 \cdot 0.5\text{H}_2\text{O}$, with Sc_2O_3 impurity.

The structure was solved in collaboration with Dr. N. Guillou, in the laboratory of Prof. G. Férey (Institut Lavoisier, Versailles) as described below, and forms part of a study of the first examples of scandium methylphosphonate framework materials[3]. The extraction of the peak positions for indexing was performed using the WinPLOTR program[4]. Pattern indexing was carried out with the computer program DICVOL04[5] from the first twenty lines, with an absolute error on peak positions of $0.01^\circ 2\theta$. A tetragonal solution was found ($a = 17.79734(8) \text{ \AA}$, $c = 5.38859(3) \text{ \AA}$) and confirmed by successful indexing of all input 60 lines. Systematic absences were consistent with the $P4_2/n$ space group, which was confirmed by a structureless whole pattern profile refinement by Topas software[6]. Subsequent structure solution calculations were performed with the EXPO package, integrating EXTRA for extracting integrated intensities and SIR97 for direct methods structure solution[7-9]. The Sc, P, Na and framework O atoms were found from the E-map with the highest figure of merit. The corresponding atomic coordinates were used as the starting model for Rietveld refinement, using the FullProf[10] program integrated in WinPLOTR software.

A pseudo-Voigt function was selected to describe individual line profiles. Unit cell and instrumental parameters were allowed to vary from time to time during the refinement process, as well as atomic

coordinates with soft distance and angular constraints. At this stage of the refinement, the structural model indicators converged to $R_B = 0.40$ and $R_F = 0.28$, which confirmed the validity of the starting structural hypothesis. Difference Fourier calculations (SHELXL²⁵) revealed unambiguously the missing carbon atoms of methyl groups and the occluded water molecule. Sc_2O_3 was considered as a second phase and its scale factor, as well as its profile factors were refined. Hydrogen atoms of methyl groups were then treated as riding by SHELXL and fixed during the Rietveld refinement. Their contribution drastically improved R_B value and C-P distances. The final Rietveld refinement carried out in the angular ranges $2-38^\circ 2\theta$ used 973 reflections. All distance and angular constraints were removed. Figure 2 shows the final fit obtained between calculated and observed patterns and figure 3 shows the structure.

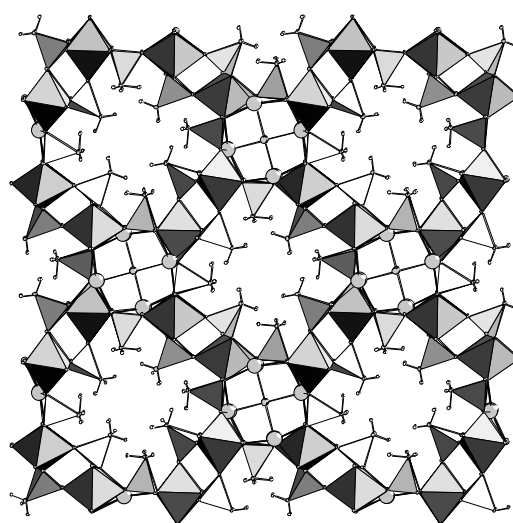


Figure 3. The structure of $\text{NaSc}(\text{CH}_3\text{PO}_3)_2 \cdot 0.5\text{H}_2\text{O}$

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