	Experiment title: Analysis of complex structures using high-resolution powder diffraction data	**Experiment number**: 01-01-265
Beamline: BM01B	**Date of experiment**: from: 4-Aug-2003 to: 7-Aug-2003	**Date of report**: 31-Mar-2004
Shifts: 9	**Local contact(s)**: Hermann Emerich	*Received at ESRF:*

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Report:

High-resolution powder diffraction data were collected on four samples during this run: the calcium potassium silicate CAS-1 (from Chun Feng Xue, Taiyuan, China), the layer aluminophosphate MDAP-3 (from A. Tuel, Villeurbanne, France), a calcined sample of an $AlPO_4$-**SOD** material (from J.-L. Paillaud, Mulhouse, France), and a calcined sample of the aluminophosphate IST-1 (from F. Ribeiro, Lisbon, Portugal).

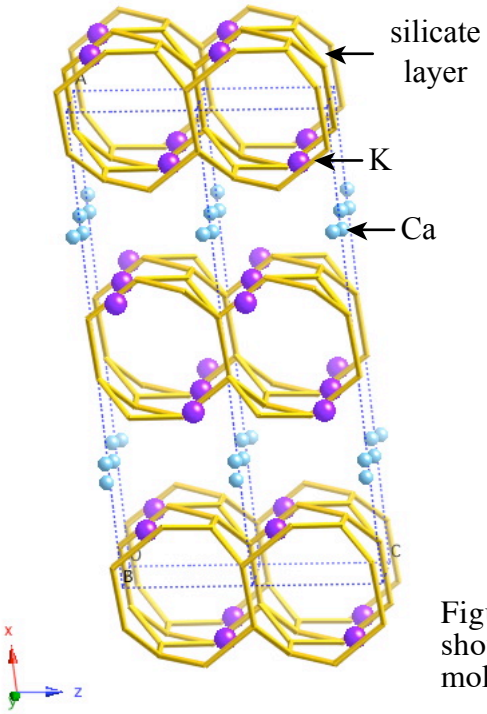

Figure 1. The structure of the calcium potassium silicate CAS-1 showing the silicate layers and the positions of the cations. Water molecules and silicate oxygens have been omitted for clarity.

The basic structure of CAS-1 (*C*2, a = 24.158 Å, b = 7.016 Å, c = 6.482 Å, β = 95.19°) was solved from data collected on a textured sample (ESRF experiment CH-1318), but high-resolution data were needed to complete and refine the structure (Figure 1). Such data had been collected in a previous experiment (01-01-265, December 2002), but the intensities proved to be distorted by an unexpected

preferred orientation of the crystallites in the capillary that could not be described with the simple function used in most Rietveld refinement programs. Therefore a new sample was prepared and remeasured during this run. Subsequent refinement of the structure using these data converged with $R_F = 0.062$, $R_{wp} = 0.175$ ($R_{exp} = 0.097$).

The approximate structure of MDAP-3 ($P2_1/c$, a = 14.080 Å, b = 8.4763 Å, c = 18.9954 Å, β = 100.95°) had been deduced from laboratory data collected on a very small single crystal, but the quality of those data did not allow a satisfactory refinement. Therefore, high-resolution powder diffraction data were collected to confirm and complete the structure. The profile fit for the current status of the Rietveld refinement ($R_F = 0.087$, $R_{wp} = 0.235$ ($R_{exp} = 0.130$)) is shown in Figure 2. The disorder at one of the two organic molecule positions between the aluminophosphate layers could not be modelled in detail.

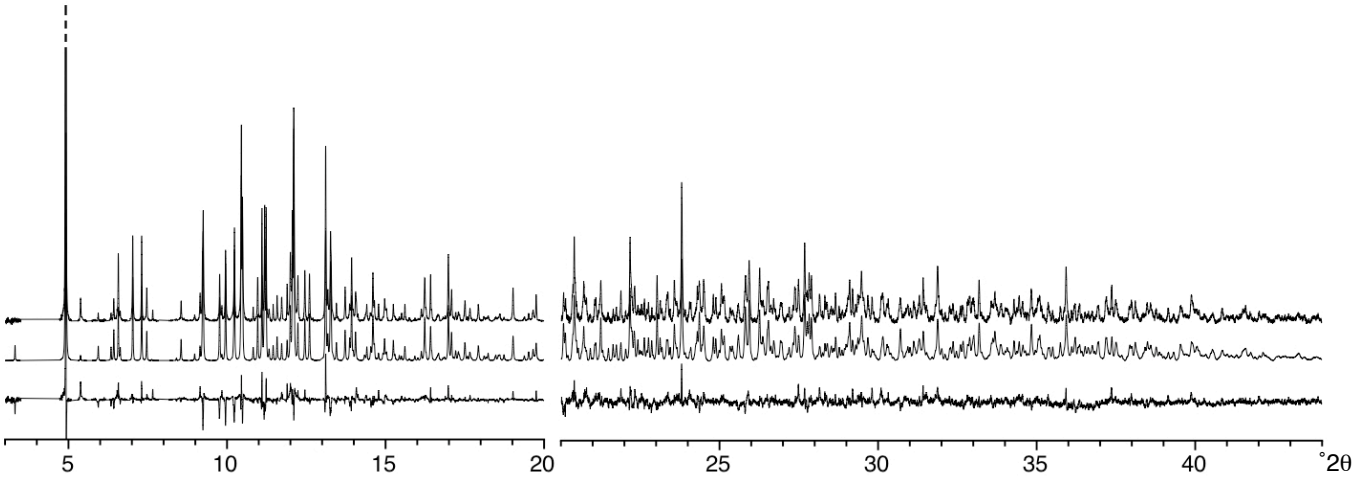

Figure 2. The observed (top), calculated (middle) and difference (bottom) profiles for the Rietveld refinement of the structure of the aluminophosphate MDAP-3. The first peak has been cut at 1/3 of its full height and the second half of the profile has been scaled up by a factor of 6 to show more detail.

In $|(C_3H_7NO)_{12}|[Al_{36}P_{36}O_{144}]$ - **SOD,** which is synthesized in the presence of dimethyl-formamide (DMF), some of the Al atoms of the framework structure coordinate to a DMF and a water molecule in addition to the four framework oxygens. As a result, the ideally cubic framework becomes monoclinic (*Cc*, a = 12.94 Å, b = 12.47 Å, c = 8.63 Å, β = 95.8°) [1]. Upon removal of water molecules, but not DMF, the *c*-axis is tripled (*Cc*, a = 12.820 Å, b = 12.183 Å, c = 26.99 Å, β = 91.4°). To elucidate the reason for this change, structure analysis of a sample dehydrated under vacuum at 100°C was undertaken. The very high quality synchrotron data revealed that the DMF molecules had rearranged themselves as the water was removed, resulting in three different kinds of sodalite cages with 9 crystallographically distinct Al and another 9 P sites. In total 275 structural parameters were refined. Refinement converged with $R_F = 0.047$, $R_{wp} = 0.045$ ($R_{exp} = 0.015$).

The calcined IST-1 sample proved to have rather broad peaks and only very low intensity beyond *ca* 20°2θ, and structure analysis has not yet been attempted. Manscripts describing the other three results are presently in preparation.

[1] L. Vidal, J.-L. Paillaud, Z. Gabelica, *Microporous Materials* 24, 189-197 (1998)