

Experiment Report Form

**Experiment title:**

Crystal structure determination of hybrid organic-inorganic allumino-silicates

Experiment number:

CH-2699

Beamline: BM1B	Date of experiment: from: 05/02/2009 to: 09/02/2009	Date of report: <i>Received at ESRF:</i>
Shifts: 9	Local contact(s): Dr. Hermann EMERICH	

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Report:

The aim of the CH-2699 experiment was the determination of the crystal structure of three new crystal hybrid organic-inorganic microporous alluminosilicates named ECS-3, ECS-5 and ECS-7. Our synchrotron measurements were performed on three as synthesized samples prepared according to synthesis route optimized in eni labs.

The high-resolution synchrotron X-ray powder diffraction patterns were collected at the beam line BM1B. The beam line was set to deliver a wavelength of 0.80175 Å for the sample named ECS-3 and 0.4990 Å for the remaining samples. Placed in borosilicate capillaries of 1.0 mm in diameter, the samples were spun during data collection in order to minimize preferred orientation. Data were collected at room temperature, in continuous mode across a range of $1 \leq 2\Theta \leq 50^\circ$, with accumulation times increasing with the scattering angle, and rebinned with a step size of $0.003^\circ 2\Theta$.

Indexing of the synchrotron powder diffraction patterns and space-group determination of all the hybrid organic-inorganic microporous alluminosilicates were achieved by using different programs, in particular ITO, TREOR and TOPAS. A subsequent profile fitting were conducted by the Le Bail method by using the GSAS-EXPGUI package and TOPAS.

In the case of ECS-3 the *ab initio* crystal structure solution was carried out by Automatic Diffraction Tomography. ECS-3 crystallizes in the monoclinic system with unit cell parameter $a \sim 19.7$, $b \sim 27.7$, $c \sim 9.5 \text{ \AA}$, and $\beta \sim 102.7^\circ$. The analysis of the systematic absences indicates C2/c or the non centrosymmetric Cc as the possible space groups. A significant portion of the ECS-3 crystal structure was readily obtained by using the Cc space group. In spite to the really good quality of the electron diffraction data, to complete and refine the ECS-3 intriguing structural model required a more completed data set. For this purpose the high resolution X-ray powder diffraction measured data was of paramount importance; using them we were able to complete and refine the ECS-3 crystal structure. This can be described by the stacking along the [100] of alluminosilicate layers developed on the (100) plane and held together by phenilene groups (Figure 1).

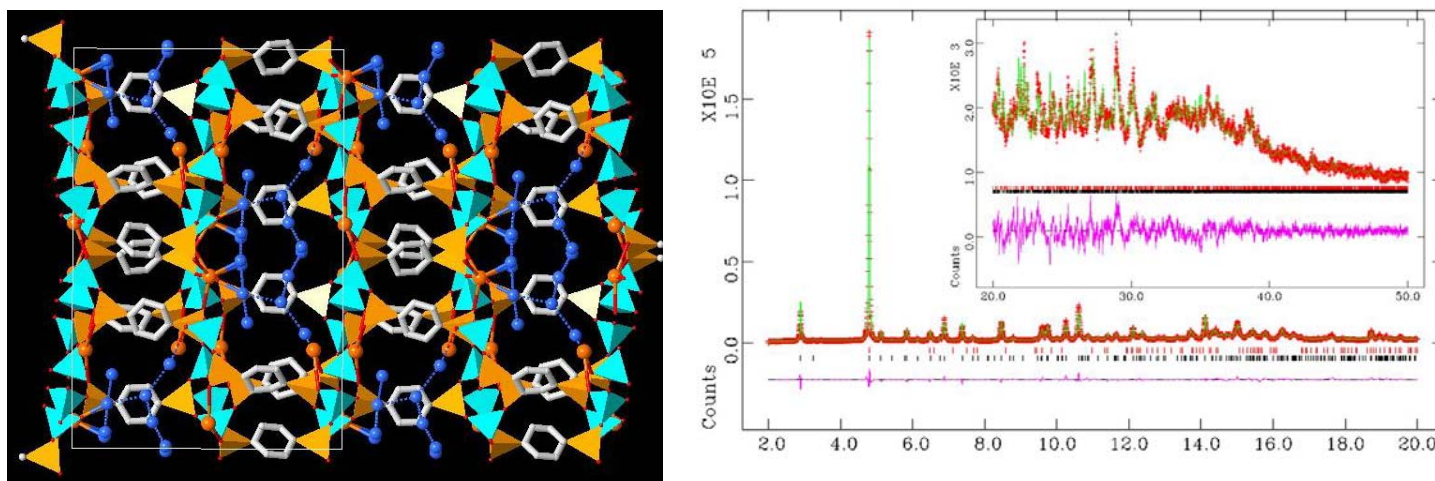


Figure 1. Left: Final crystal structure for ECS-3 sample as viewed along the [001]. Polyhedra: orange (SiO₃C), light blue (AlO₄). The extraframework content is also shown as spheres: orange Na, blue H₂O. Right: Rietveld plot of the final refinement cycle, $RF^2 = 7.7\%$, $R_p = 6.2\%$, $R_{wp} = 8.2\%$.

In the case of ECS-5 and ECS-7 a tetragonal and an orthorhombic unit cell were obtained, respectively. Concerning ECS-5 the unit cell has parameters $a = b \sim 10.22 \text{ \AA}$, $c \sim 71.51 \text{ \AA}$. The analysis of the systematic extinctions, performed using the space group search routine implemented in EXPO2009 gave the highest figure of merit for I41/acd. Regarding ECS-7, the unit cell parameter obtained by TOPAS were $a \sim 36.56$, $b \sim 13.27 \text{ \AA}$, $c \sim 9.63 \text{ \AA}$. The same software proposed the Immm as the possible space group.

The Le-Bail profiles fitting seem to confirm the correct assignment of both the space groups (Figure 2). The ECS-5 and ECS-7 crystal structures determination using this information is in progress, yet.

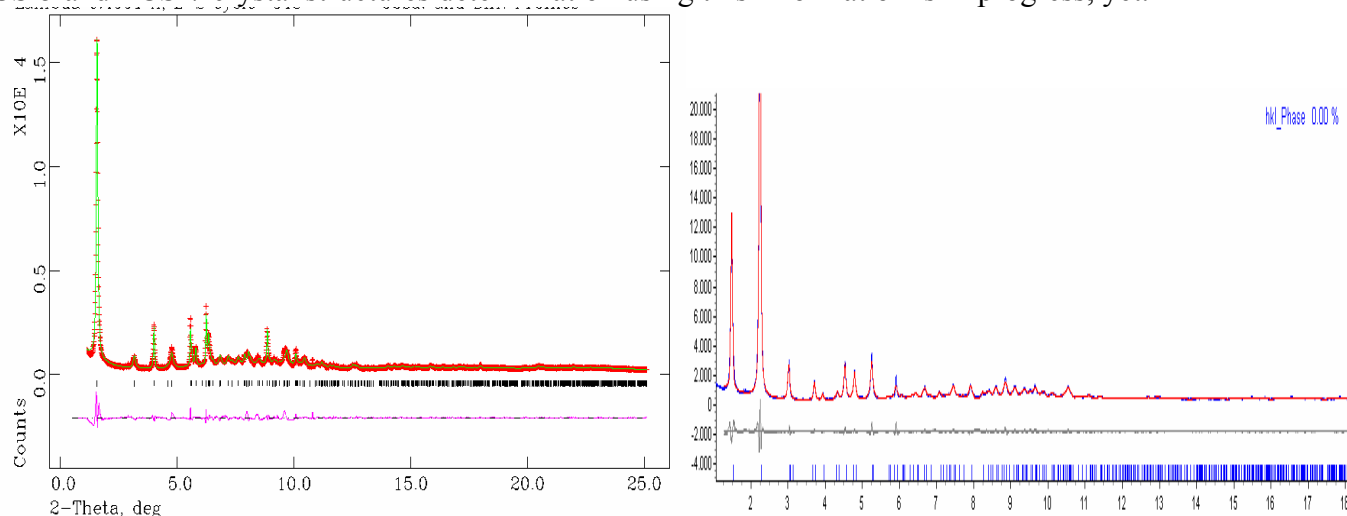


Figure 1. Portion of the final GSAS profile fitting for ECS-5 seems confirms the correct assignment of the I41/acd space group. Portion of the final TOPAS profile fitting for ECS-7 seems confirms the correct assignment of the Immm space group.