X	**Experiment title:** Analysis of complex structures using high-resolution powder diffraction data	**Experiment number**: 01-01-694
Beamline: BM01B	**Date of experiment**: from: 4-Oct-2005 to: 7-Oct-2005	**Date of report**: 31-Aug-2006
Shifts: 9	**Local contact(s)**: Hermann Emerich	*Received at ESRF:*

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Report:

During this experiment, high-resolution powder diffraction data were collected on the zirconium phosphate ZrPO-Pyr phase ((|$(C_5H_6N)_4(H_2O)_2$|[$Zr_{12}P_{16}O_{60}(OH)_4F_8$]) at a wavelength of 0.80062 Å. The pattern could be indexed on an orthorhombic unit cell (*Pnnm*, a = 15.148 Å, b = 19.170 Å, c = 6.621 Å), and the structure was then solved by direct methods using the program EXPO [1]. Refinement of the structure converged with the *R*-values R_{F2} = 0.068 and R_{wp} = 0.127 (R_{exp} = 0.075). However, one of the phosphate groups and the pyridinium ions appeared to be disordered in the space group *Pnnm* (see Figure 1), so several different subgroups that would allow ordering were explored. None of these produced either a better geometry or a better profile fit

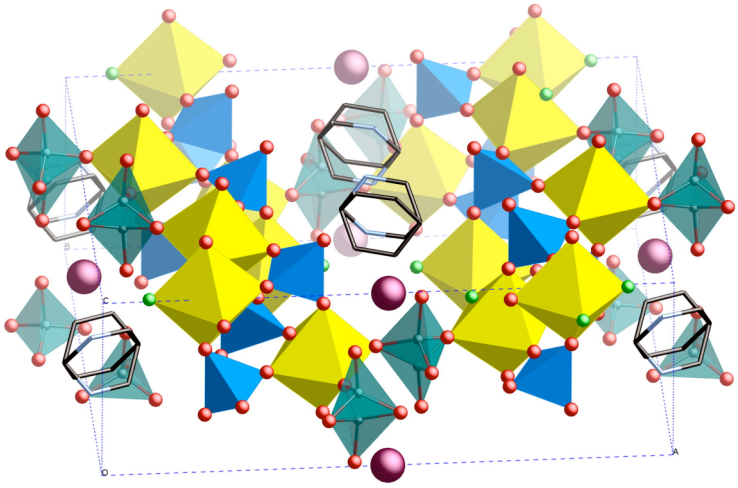

Figure 1. The structure of ZrPO-Pyr in the space group *Pnnm* (Zr: yellow, P: blue and teal, O: red). Note the disorder in the teal-colored PO_4 groups in the pyridinium ions.

(Figure 2), so it was concluded that the structure is in fact partially disordered. A subsequent examination of the literature showed that the (single-crystal) structure of a closely related material made with 2,2-dimethyl- 1,3-diaminopropane instead of pyridine exhibits a similar disorder of this PO_4 group [2].

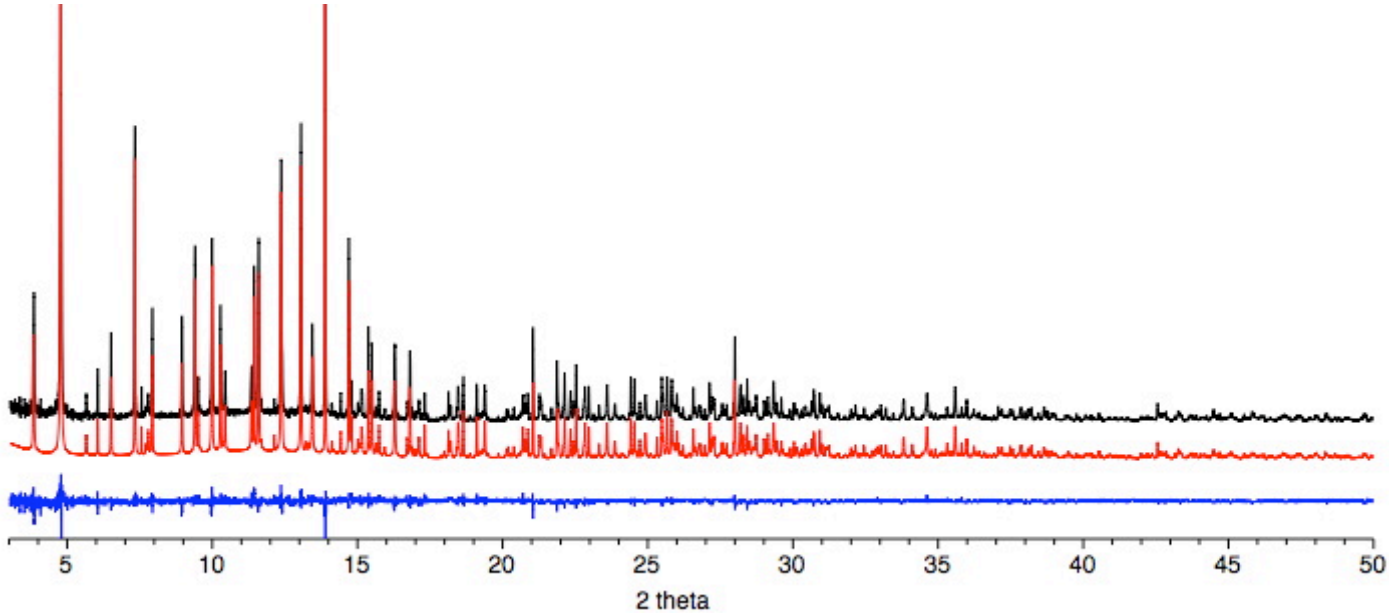

Figure 2. Observed (black), calculcated (red) and difference (blue) profiles for the Rietveld refinement of ZrPO-Pyr (λ = 0.80062 Å).

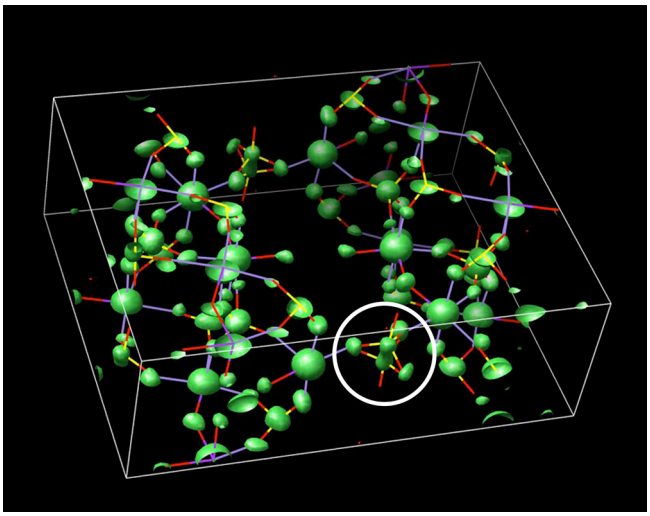

Figure 3. Electron density map from *Superflip* showing the disorder of the PO_4 group (circled) in the ZrPO-Pyr phase.

To double-check that the correct symmetry had not been overlooked, the structure solution program *Superflip* [3], which is based on the charge-flipping algorithm of Oszlányi and Süto [4] and has been newly modified to accom-modate powder diffraction data [5], was applied. The alogrithm operates in *P*1, and makes no assumptions regarding symmetry. The resulting electron density map (Figure 3) clearly shows the disorder of the PO_4 group.

The data collected on three alumino-phosphate phases synthesized with different organic structure directing agents will be used for further testing of this very promising algorithm.

References

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