

**[o.m3.o1] In-situ studies of hydrothermal synthesis of microporous materials.** P. Norby, *Department of Chemistry, University of Oslo, N-0315 Oslo, Norway*  
 Keywords: microporous materials.

Time resolved *in-situ* powder diffraction is a powerful tool for studying synthesis and chemical reactions involving crystalline material. By using high intensity synchrotron X-ray radiation, a time resolution of the order of seconds is obtainable. The collected powder diffraction patterns are of sufficient quality to allow kinetics data and real time structural information to be extracted.

By using a capillary based micro reaction cell<sup>1,2</sup>, a number of studies of hydrothermal crystallization of microporous and layered materials have been performed. Results from some of these studies will be presented, including:

- Studies of the role of the substituting element on crystallization kinetics and energetics in hydrothermal synthesis of transition metal substituted microporous aluminophosphates<sup>1</sup>.
- Chemistry at high pressure; a study of hydrothermal synthesis of microporous and layered materials at high pressure.
- Simultaneous high resolution and medium resolution time resolved powder diffraction: Determination of crystallite size and crystallization kinetics in hydrothermal synthesis.
- Initial *in-situ* experiments in connection with studies of hydrothermal crystallization of zeolites in microgravity: Using combined *in-situ* synchrotron X-ray powder diffraction and Dynamic Light Scattering (DLS) in studies of crystallization of zeolites from clear solutions.
- *In-situ* powder diffraction studies of hydrothermal crystallization of microporous materials using conventional X-ray radiation.

**[o.m3.o2] The Influence of Fluoride Ions on the Structure, Symmetry and Thermal Properties of Siliceous Zeolites.** R.E. Morris, *School of Chemistry, University of St. Andrews, Purdie Building, St. Andrews KY16 9ST, UK*

Keywords: microcrystal X-ray diffraction, zeolites, template ordering

Since the advent of microcrystal diffraction stations at the synchrotron sources in Daresbury and Grenoble we have been able to obtain high quality structural information on microporous materials, which previously could only be studied using powder methods. This lecture will include some recent results obtained at the Daresbury synchrotron source (Station 9.8), where we have studied the influence of fluoride ion mineralisers on the structure and symmetry of zeolites and their thermal properties, such as negative thermal expansion.

The results to be described may have great importance in how nonlinear optical (NLO) solids can be prepared. The need for polar solids for use as NLO materials has led to numerous attempts to incorporate interesting organic molecules inside the pores and cavities of zeolites and other microporous materials. The major advantage of this approach is the combination of inorganic frameworks with optically active organic molecules to produce very robust functional materials with many potential applications. A major obstacle to this work is the need for the final material to crystallize in a non-centrosymmetric spacegroup in order to be an active NLO material. This lecture describes how fluoride, added as a mineraliser to a zeolite synthesis, leads to crystallization in a polar non-centrosymmetric spacegroup for zeolite IFR, a framework whose topological symmetry is centrosymmetric and therefore nonpolar. This also leads to a non-centrosymmetric ordering of the organic template molecule in the channels, which is vital if materials with good NLO properties are to be prepared. The reasons for this ordering can be traced to the influence of the fluoride ion on the structure of the framework. When the fluoride ions and templates are removed by calcination, the framework symmetry is centrosymmetric.

[1] Norby P., "Synchrotron powder diffraction using Imaging Plates; Crystal structure determination and Rietveld refinement" *J. Appl. Cryst.*, 1997, 30 : 21-30

[2] Norby P., "Hydrothermal Conversion of Zeolites: An *In-situ* Synchrotron X-ray Powder Diffraction study", *J. Amer. Chem. Soc.*, 1997, 119 : 5215 -5221.

[3] Norby P. et al. "Crystallization in nonaqueous media of Co- and Mn-substituted microporous aluminophosphates investigated by time resolved *in-situ* synchrotron powder diffraction" *Inorg. Chem.*, 1999, 38 : 1216-1221.