ESRF	**Experiment title:** High Resolution PXRD Studies of Nanoporous Metal-Organic Frameworks Under Pressure and Temperature	**Experiment number**: CH-2505
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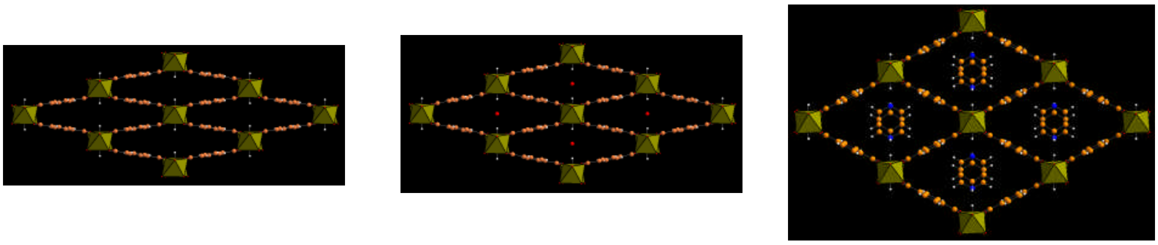
Report:

Our aim was to use high resolution powder X-ray diffraction to investigate the atomic-scale structures of nanoporous metal organic framework materials as a function of temperature and applied pressure for the first time. These materials already have known 'breathing' properties upon introduction of organic guest molecules and we anticipated that their behaviour under pressure and temperature would reveal some unusual results, with large positive or large negative thermal expansion coefficients and the uptake of large amounts of small molecules under pressure. This study will further the understanding of the sorption properties of this important family of materials.

Metal organic framework materials have now established themselves as a family of materials whose properties in separation and sorption of small molecules can out-perform the long-established zeolites.[1-4] Current investigations are taking place into their application in important contemporary areas such as CO_2 and H_2 sorption, of great relevance to the world today. The MIL-*n* family of solids are one example of such materials, and they have quite unique properties: for example, they have the highest total surface areas of any crystalline material (up to 6000 m^2g^{-1})[2, 5, 6] and show a reversible 'breathing' effect upon the introduction of guest molecules into their porous structrures,[7, 8] involving atomic displacements of several Ångströms. Their structures are made up of inorganic metal-oxy/metal-hydroxy clusters connected by organic linkers, and the overall connectivity of the structures is maintained during the breathing process.

Although the room temperature structures of a number of these materials are known (both in the as-made form and with the presence in guest molecules) and have been well characterised using powder diffraction methods, no studies of their structures and properties as a function of temperature and/or pressure have yet been undertaken . This is important to study in order to better understand their sorption properties, in particular to understand the limits of the flexibility of the framework structures, but we also anticipate more fundamental results of interest to the wider solid-state community. This is because their structures are made up of rigid building units, connected by organic linkers and the chemical bonds between the two can act as by flexible 'hinges': this suggests that for materials that possess anisotropic structures (one-dimensional channel systems, for example) we will see severely anisotropic thermal expansivity, perhaps even negative thermal expansion in one or more direction. Negative thermal expansion is now well-established in silicate zeolite materials,[9] and appears to be the usual effect, rather than being a curiosity.

We therefore studied three materials with the MIL-53 type structure. These are Fe(III) benzene-dicarboxylates that consist of a one-dimensional chain motif made up of *trans*, corner-linked iron octahedra, cross-linked by the bidentate carboxylate to yield an open structure with parallel, one-dimensional channels running along c. This material can be made with a variety of different guest molecules, and in each case the organic guest is ordered, held by strong host-guest and guest-guest interactions. Figure 1 shows the structures of the three materialz we studied, an anhydrous form, one with water as guest molecules, and one with pyridine: these are the room temperature structures, solved from the data recorded during this run.



anhydrous $V = 904.42$ Å3

+ H_2O $V = 1000.54$ Å3

+ pyridine $V = 1395.95$ Å3

Figure 1: MIL-53, an iron(III) terephthalate made up of infinite chains of {FeO_6} octahedra cross-linked by terephthalate bridges: the addition of various guest molecules causes a reversible breathing.

We measured data from all three materials as a function of temperature using the nitrogen cryostream on ID31. At the current stage, just two month after the experiment, we have refined unit cell parameters for each of the materials. Figure 2 shows the values obtained for MIL-53(Fe), H_2O.

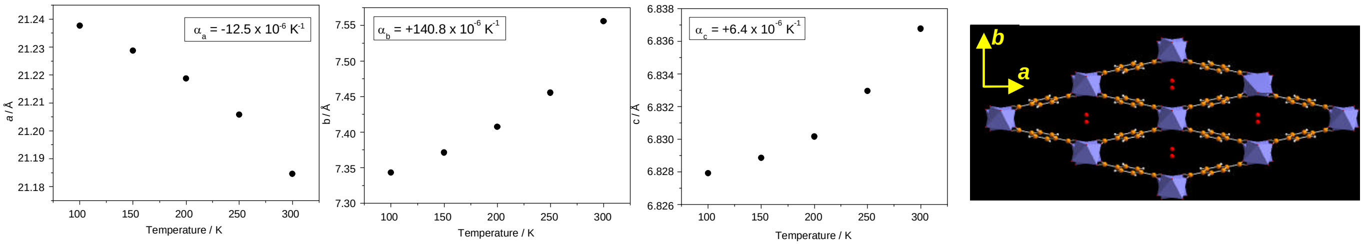


***Figure 2: Thermal variation of cell parameters for MIL-53-Fe(H_2O). The structure is shown viewed along* c**

The *b* cell parameter shows a dramatic expansion with temperature. This corresponds approximately to the short diagonal of the lozenge-shaped pores. The magnitude of the thermal expansion coffecient is large: indeed such a value has only very recently (February 2008) been reported for metal cyanide network structures by Goodwin *et al.* and has been termed 'colossal'.[10] The *a* parameter shows a shortening on heating: this is clearly in response to the large increase in *b*, since it is related to the long diagonal of the lozenge-shaped pores. The *c* parameter, whcih corresponds the inorganic backbone of the MOF structure shows a comparatively small positive thermal expansion coeffient: almost 1/20 of the value for **b**. This reflects the comparative rigidity of the inorganic chains. The highly anisotropic behaviour reflects the the anisotropic crystal structure of MIL-53, and in fact the thermal behaviour mimics the structural response of the material to the introduction of a wide-variety of guests.[11]

We are currently refining the structures of all materials at each temperature, in order to determine an atomic-scale model for the thermal flexibility of these materials. We then intend submitting a publication on this area, as it represents one of the first experimental studies of the therma expnasivity of MOFs.

We also studied the behaviour of MIL-53 in the pressure of excess water under pressure using the pressure cell, [12, 13] and also on heating in sealed capillary to generate autogeneous pressure. In both cases no 'super hydration' of MIL-53 was observed and the framework remained in a semi-open form. We have recently verified this at higher pressures using a hydrothermal autoclave at the SRS.[14]

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