

# The synthesis and structure solution of UiO-7, a new molecular sieve

Duncan E. Akporiaye,<sup>\*a</sup> Helmar Fjellvag,<sup>b</sup> Erling N. Halvorsen,<sup>b</sup> Jorunn Hustveit,<sup>b</sup> Arne Karlsson<sup>a</sup> and Karl P. Lillerud<sup>\*b</sup>

<sup>a</sup> SINTEF Chemistry, PO Box 124 Blindern, N-0314 Oslo, Norway

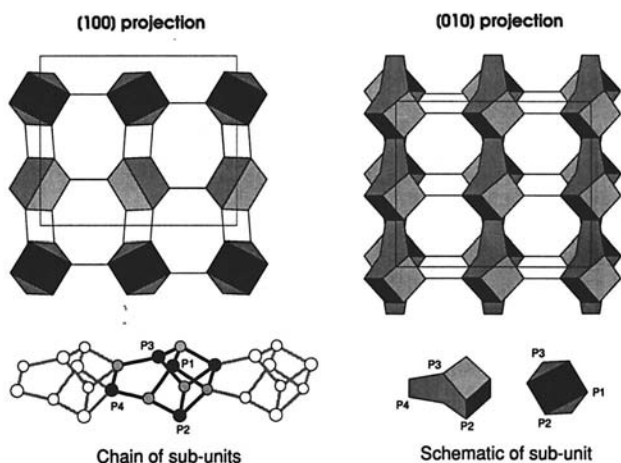
<sup>b</sup> University of Oslo, Department of Chemistry, PO Box 1033 Blindern, N-0315 Oslo, Norway

**A new molecular sieve type material UiO-7 is prepared and the structure solved through a combination of simulated annealing, used to isolate the framework topology, and high-resolution synchrotron X-ray powder diffraction, for the location of the non-framework atoms.**

One of the goals in the hydrothermal synthesis of zeolites and metalloaluminophosphates is the identification of new synthetic parameters that result in novel phases which may be then isolated in a pure form. The introduction of fluoride into known synthetic recipes<sup>1</sup> has opened up new possibilities which in our case has resulted in the formation of a new aluminophosphate UiO-7, the structure of which has been solved through a combination of recent methods based on simulated annealing and high-resolution synchrotron diffraction data.

UiO-7 was synthesised from a fluoride modified aluminophosphate gel containing the organic amine tetramethylammonium hydroxide (TMAOH). This system, in the absence of the fluoride, usually forms AlPO<sub>4</sub>-20,<sup>2</sup> an aluminophosphate variant of the mineral sodalite. The synthesis was carried out from a gel having a molar oxide ratio of 1 Al<sub>2</sub>O<sub>3</sub> : 1 P<sub>2</sub>O<sub>5</sub> : 0.2 HF : 1 TMAOH : 50 H<sub>2</sub>O. The gel was prepared in Teflon liners in which pseudoboehmite was first mixed with water and phosphoric acid. The amine was then added followed by HF after which the gel was well stirred. The liners were put in stainless-steel autoclaves and heated in an oven at 150 °C for 21 h, after which they were quenched in cold water and the microcrystalline product separated, washed with water and dried.

High-resolution powder diffraction data were collected for the as-synthesised sample at the Swiss Norwegian beamline (D1) at the European Synchrotron Radiation Facility (ESRF). Indexing of the diffraction pattern<sup>3</sup> identified an orthorhombic unit cell ( $a = 7.266$ ,  $b = 15.333$ ,  $c = 16.592$  Å) and a study of

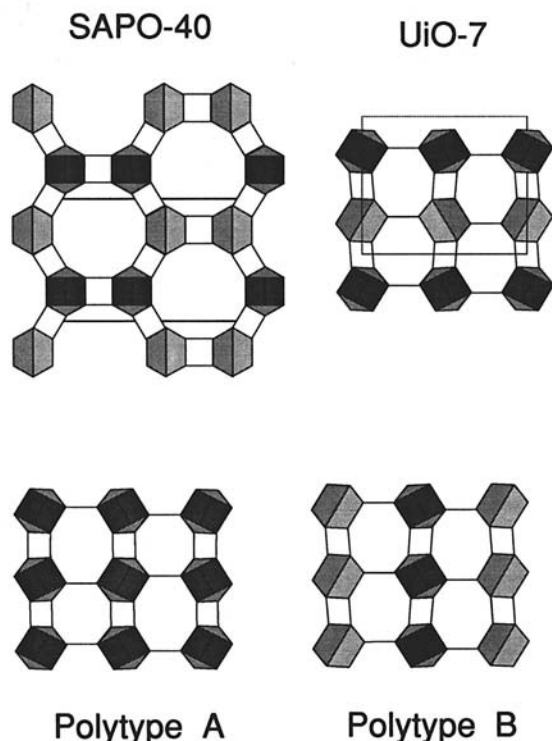


**Fig. 1** The framework of UiO-7 showing details of the constituent sub-units and their formation into chains and [100] and [001] projections of the framework along the two main eight-ring channels

systematic absences indicated two possible primitive space groups *Pbcm* and *Pbc2<sub>1</sub>*.

The topology of the framework was determined through simulated annealing (SA)<sup>4</sup> in which a series of framework topologies are generated within the symmetry of the space group according to a figure of merit based on deviations from prescribed connectivities, bond lengths, bond angles and match with the observed powder diffraction pattern. The total number of tetrahedral atoms ( $N_T$ ) of the framework was determined as 32, from the correlation of the micropore volume and the framework density.<sup>5</sup> The number of unique T sites in the asymmetric unit ( $N_U$ ) was estimated as 4 or 6 from the <sup>31</sup>P solid-state MAS NMR spectra of the calcined and as-synthesised materials.

The SA runs within the two possible space groups and using the two values of  $N_U$  resulted in the generation of only one feasible topology. Subsequent geometry optimisation<sup>6</sup> within the calcined unit-cell dimensions gave a simulated powder diffraction pattern having an almost perfect match with the observed data, indicating that the correct structure had been found. However, in order to take account of the Al/P ordering in the framework, the mirror plane of the *Pbcm* space group had to be removed, resulting in *Pbca* symmetry and a doubling of the unit cell along the *a* axis.



**Fig. 2** Alternative means of linking the sub-unit to form SAPO-40, and two other theoretical topologies related to the UiO-7 framework

As is clear from the [100] and [010] projections of the framework (Fig. 1), UiO-7 has a two-dimensional eight-ring channel system. The framework is built up of a rather unusual cage-like unit which we have also identified in the recently discovered structure of SAPO-40.<sup>7</sup> In UiO-7, these units are connected together in chains which run parallel to the *a* axis. Adjacent chains are tilted, having the same orientation along the *c* axis, and opposite orientations along the *b* axis. In SAPO-40, these chains are not tilted with respect to each other, with the resulting interconnections forming a twelve-ring channel system. The simple means by which these chains interconnect also suggest alternative hypothetical polytypes of the SAPO-40 and UiO-7 framework topologies, for example, as shown in Fig. 2, that in which all chains in UiO-7 have the same orientation

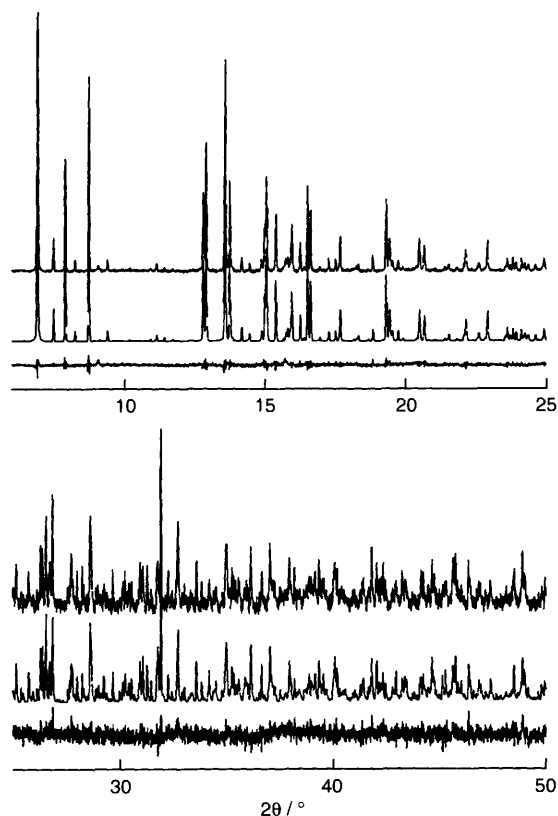


Fig. 3 Results from the Rietveld refinement of synchrotron data from UiO-7: observed (upper), calculated (middle) and difference (lower)

along both *b* and *c* directions (polytype A) or they alternate in orientation along the *c* instead of *b* direction (polytype B).

A detailed structural analysis was carried out on the as-synthesised materials, to confirm the structural model and to locate all non-framework atoms. The geometric optimised coordinates within the new enlarged unit cell were used as input into the Rietveld refinement of the high-resolution XRD data.<sup>8</sup> Difference Fourier map calculations gave atomic coordinates for TMA and located the fluorine anions within the cage-like sub-unit, accommodated between two five-coordinate Al atoms. The final set of parameters gave a profile *R*-factor  $R_p = 0.061$ , the resulting data fit from the refinement is given in Fig. 3.

The discovery of UiO-7 shows the continued potential for the preparation of novel phases through modification of known gel systems. The solution of the structure by simulated annealing and high-resolution PXRD in combination with detailed physical characterisation shows the potential for new methods in the solution of complex structures from powder data.

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