MS10.10.05 A COMBINATORIAL METHOD OF GENERATING PERIODIC TETRAHEDRAL FRAMEWORKS M. M. J. Treacy, K. H. Randall, S. Rao, J. A. Perry, D. J. Chadi, NEC Research Institute, Inc., 4 Independence Way, Princeton, NJ 08540

A combinatorial method for generating periodic 4-connected frameworks is described. The computer algorithm requires, as input, the number of unique tetrahedral atoms and the crystallographic space group type. The algorithm then searches systematically over all possible combinations of connected crystallographic sites that are consistent with 4-connected nets. The resulting graphs are then relaxed by simulated annealing to identify the regular tetrahedral zeolite topologies

Results are presented for one unique tetrahedral atom in each of the 230 crystallographic space group types. 5,043 unique 3-dimensional 4-connected uninodal graphs are found. About 3% of these graphs refine to reasonable tetrahedral topologies. All the known uninodal zeolites, and dense silicon dioxide phases are identified, and many (if not all) of the previously known hypothetical uninodal frameworks are found. A number of new dense and microporous frameworks are described. There is a combinatorial explosion of graphs as the number of unique vertices is increased, a result which currently restricts this method to consideration of small numbers of unique atoms.

We also highlight idiosyncrasies in the International Tables for Crystallography concerning the descriptions of the asymmetric units. Topological discrepancies arise when comparing enantiomeric pairs of space group types.

MS10.10.06 THE NEW OPEN FRAMEWORK $Na_x[(V^{IV}O_2)_2(V^{V}(O,OH))_{0.5}\ PO_4](PO_4)_y(OH)_{x-1.5-3y}\ .\ ZH_2O$ (WITH x=1.5-2.0, y=0-0.17, z=3-4). M. Schindler, W. H. Baur, Inst. für Kristallographie, Goethe-Universität, Senckenberganlage 30, 60054 Frankfurt am Main, Germany

The title compound (short: FVP-1) is one of a new class of frameworks that are more open than all aluminosilicates and Al- or Ga-phosphates known so far. These frameworks exchange ions and their H_2O can be reversibly removed. FVP-1 was grown hydrothermally in the Na/V/P/-H_2O/tetraethylamine system (473K). It crystallizes in space group Im3m with a=16.025Å. It contains $V^{IV}_4V^{V}O_9(PO_4)_{4/2}$ groups made up of 5 square pyramidal coordinations of O atoms around V in the shape of a spiked helmet, where the spike is the V=O group of the central V^{V} co-ordination polyhedron. These molecules are statistically arranged around mirror planes. In contrast to the Müller-Döring-type (**1**) Keggin molecule, e.g. $V_{18}O_{42}(SO_4)$, the tetrahedral groups are placed here **outside** of the shell of square pyramidally coordinated V atoms and thus are able to form bridges to neighboring molecules. We call them **anti-Keggin molecules.** The framework formed by the $V^{IV}_4V^{V}O_9(PO_4)_{4/2}$ molecules is best visualized by recalling the net on which the crystal structure of NbO is based [Wells, (**2**)]. The mean free channel diameters measure about 4.1Å and the framework density is 10.2 V and P atoms/1000 Å. Thus FVP-1 and two other recently found microporous frameworks (**3**), are the most open framework described so far. FVP-1 does not collapse when dehydrated, and is stable up to 623 K. The size of the pores in the framework is large, because its building unit, $V^{IV}_4V^{V}O_9(PO_4)_{4/2}$, is of low symmetry and already large in itself. V^{IV}/V^{V} compounds are known to be potentially useful as catalysts. It can be expected that other phases based on the same principle can be synthesized under similar conditions.

(**1**) A. Müller and J. Döring, *Z. anorg. allg. Chem.*, 1991, **595**, 251.
(**2**) A. F. Wells, *'Structural Inorg. Chem.* '' Oxford Univ. Press, 1993.
(**3**) M. I. Khan et al., *Chem. Mater.*, 1996, **8**, 43.

PS10.10.07 STRUCTURAL STUDIES OF DAF-4. [a]P.A. Barrett and [b]R.H. Jones. [a]The Royal Institution of GB, 21, Albemarle St, London W1X 4BS, UK. [b]The University of Keele, Keele, Staffordshire ST5 5BG, UK.

The current work describes the structure solution of a new Levyne Cobalt substituted aluminophosphate (CoAlPO) analogue by single crystal methods. This new sample of CoAlPO-35 was synthesised hydrothermally from a nutrient gel containing sources of Al, P and Co employing the new template 2-methylcyclohexylamine as the structure directing agent. The unit cell showed there to be a doubling of the c axis compared to Levyne. This structure is known consistent with the strict Al and P alternation expected in an aluminophosphate.

Coordinates for the initial starting model were taken from Levyne. The space group is R-3c a=13.317(3)Å c=45.921(9)Å. This produces 4 crystallographically distinct tetrahedral framework sites. After successful refinement of the framework, the template (2-methylcyclohexylamine) was located using standard Fourier techniques. At this point it was observed that the Al-O bond distances were longer than expected consistent with the partial substitution of Co in place of Al. It proved possible to refine individual cobalt occupancies on these sites, which were consistent with the variation in bond length.

PS10.10.08 TIME RESOLVED CRYSTALLOGRAPHY OF GUEST/HOSTCOMPOUNDS: MOLECULAR RECOGNITION AND PHASE TRANSITIONS IN SODALITES $M[SiO_2]_6$. J. Felsche, P. Behrens*, C. Braunbarth, W. Bührer***, G. Engelhardt**, P. Fischer***, G. Van De Goor*. *Dept.Chemistry, University of Konstanz, D-78434 Konstanz, Germany; **Ludwig-MaximiliansUniversity, D-80333 München, Germany; ***University of Stuttgart, D-70550 Stuttgart, Germany; ETH-Zürich & Paul Scherrer Inst., CH-5232-Villigen, Switzerland

There is a limited number of five molecules M known so far which direct the sodalite structure via molecular recognition in hydrothermal and H_2O-free syntheses conditions[1]. The cubic host structure of the SiO_2-SOD-phases, which are well characterized by X-ray and neutron diffraction data, show unlike all the other clathrasil-types no 5-membered but instead 4- and 6-membered rings on the microporous tetrahedral framework structure. We have chosen this group of model clathrasils in order to focus our attention to the crystallography of the organic molecules M of low symmetry which, trapped in the $4^6 6^8$-SOD-cages and isolated by the 3D-periodic SiO_2-matrix, cause a typical pattern of multi-stage phase transitions into the host structure as shown by DSC-microcalorimetry and synchrotron powder diffraction data. We report here on the experimental results of three spectroscopic methods IR-spectrocopy, quasi-elastic neutron scattering and MAS-NMRspectroscopy of the nuclei ^1H, ^{13}C, ^{29}Si which reveal the guest/guest- and as well the guest/host-interactions through different time windows of frequences 10^{12} to 10^{15} cps, 10^8 to 10^{12} cps and 10^4 to 10^8 cps, respectively. Starting from the frozen in disorder statistics at 10K up to the critical temperatures of about 800K, where thermal decomposition and/or oxidation of the guest molecules occurs, structural phase transitions at temperatures T_{st} and as well glass points T_g demonstrate critical characters in the van der Waals guest/host-interactions of molecular recognition.

[1]C.Braunbarth *et. al.; Zeolites* 1996 16 207-217.