

RESULTS AND DISCUSSION. As described in the summary, the cobalt atom is octahedrally coordinated to five framework oxygen atoms and to one nitrogen atom from the organic molecule at bond distances from 1.991(1)Å to 2.136(1)Å. The average deviation of the bond angles from the ideal octahedral geometry is 7.1° and indicates relatively high distortion of the octahedron. The Al - O distances in the coordination tetrahedra are in the range of 1.727(1)Å to 1.750(1)Å and the bond angles from 107.2(1)° to 112.3(1)°. Tetrahedral P - O distances have values from 1.511(1)Å to 1.554(1)Å and the bond angles from 106.6(1)° to 113.4(1)°. The ethylenediamine molecule is in a protonated form to compensate negatively charged framework. One nitrogen atom N(1) is, as already mentioned, coordinated to cobalt atom and the other N(2) is stabilized, forming a weak hydrogen bond with O(3) atom (the distance N(2) - O(3) is 2.89(2)Å). The examination of contact distances shows no other significant contacts.

REFERENCES. (1) S. T. Wilson, E. M. Flanigen, (1986). US Patent 4. 567. 029, (2) B. Krausheer-Czarnetzki, W. G. M. Hoogervorst, R. R. Andrea, C. A. Emeis, W. J. Stork: J. Chem. Soc. Faraday Trans., 1991, 87(6), 891-895.

MS-08.02.07. STRUCTURE AND PHASE TRANSITION OF ORTHORHOMBIC $\text{AlPO}_4\text{-5}$. By N. Ohnishi*, T. Kajitani, O. Terasaki+, S. Qiu++ and K. Hiraga, Institute for Materials Research, Tohoku University, Sendai 980, Japan. *Department of Physics, Faculty of Science, Tohoku University, Sendai 980, Japan. ++Department of Chemistry, Jilin University, Changchun 130023, China.

The molecular sieve $\text{AlPO}_4\text{-5}$ is one in a new family of crystalline, microporous aluminophosphate molecular sieves. The $\text{AlPO}_4\text{-5}$ phases can be synthesized with numerous kinds of structure directing agents (templates), and they all show the same hexagonal structure. Recently, we synthesized a new type phase similar to the $\text{AlPO}_4\text{-5}$ using a synthesis medium containing fluoride anions and tropine as a template. The new phase has an orthorhombic symmetry. Crystal structure of the new phase was investigated by means of powder X-ray diffraction (XRD).

Rietveld analysis of the XRD pattern indicated that the basic arrangement of framework atoms of the as-synthesized specimen is similar to that of the known hexagonal $\text{AlPO}_4\text{-5}$, but has an orthorhombic unit cell with space group symmetry Ccc2 and lattice parameters of $a = 13.78 \text{ \AA}$, $b = 23.33 \text{ \AA}$ and $c = 8.44 \text{ \AA}$. From the XRD study at various temperatures between room temperature and 823 K, a reversible change of the symmetry from orthorhombic to hexagonal and vice versa was observed at temperatures around 400 K. Details of the crystal structure of both orthorhombic and hexagonal phase, and of the transition between them will be reported.

MS-08.02.08 DISORDER IN CLATHRASILS: X-RAY ANALYSIS OF THE XE CONTAINING CALTHRASILS DODECASIL 3C AND MELANOPHLOGITE by B. Marler*, S. Ohmann, H. Gies Inst. f. Mineralogie, Ruhr-Universität Bochum, 463 Bochum, Germany

Clathrasils are host-guest compounds with host composition SiO_2 and neutral guest molecules occupying cage-like voids. They belong to the class of porous tectosilicates and are closely related to zeolites. The formation of the porous SiO_2 framework requires the presence of the guest molecules during synthesis where they act as templates.

In the clathrasils dodecasil 3C, $136 \text{ SiO}_2 \cdot n \text{ M}^{12} \cdot m \text{ M}^{16}$, and melanophlogite, $46 \text{ SiO}_2 \cdot p \text{ M}^{12} \cdot q \text{ M}^{14}$, the Xe-atoms occupy 12-hedral (M^{12}), 14-hedral (M^{14}), and 16-hedral (M^{16}) cage-like voids with occupancies m, n, p, and q. Whereas Xe fits tightly the 12-hedra in dodecasil 3C and melanophlogite, the atom is dynamically disordered in the 14- and 16-hedral cages. For the refinement of the structures the disorder of the guest atom was considered refining multiple sites, occupancies and anisotropic thermal parameters.

PS-08.02.09 ZEOLITE STRUCTURE DETERMINATION BY SOLID STATE MAS NMR AND SYNCHROTRON POWDER DIFFRACTION. By G.T. Kokotailo^a, C.A. Fyfe^a, H. Gies^b, D.E. Cox^c, Y Feng^a, B. Marler^{b*}

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Zeolites are a relatively new class of compounds which have found extensive use as catalysts, sorbents, catalyst supports and ion exchangers. They are aluminosilicate framework structures with uniform micropore systems. The unavailability, in most cases, of good large crystals precludes single crystal structure analysis. Rietveld refinement of high resolution synchrotron powder diffraction data obtained from very highly crystalline zeolite samples yields considerable average structure information as the techniques are sensitive to long range ordering.

The application of high resolution solid state MAS NMR has emerged as a very useful and complimentary technique to x-ray diffraction. The ^{29}Si MAS NMR spectra of high silica zeolites consist of sharp highly resolved resonances whose number and intensity are related to the number of independent atoms in the structure and the relative population of the local magnetic environment of the T-atoms, and are very sensitive to any change due to defect, temperature or sorbed species. A change in symmetry will yield spectra reflecting the number and occupancy of the independent T-atoms.

The application of two dimensional solid state NMR techniques has provided a wealth of information on the connectivities of the atoms which define the three dimensional structure.

1D and 2D solid state NMR has played an essential role in the resolution of a number of zeolite structures using powder diffraction and Rietveld refinement. In this report we will discuss symmetry changes in ZSM-5, -11, and -12 due to temperature and sorption induced phase transitions, pseudo symmetry and super structure and how these effects influence the local geometry of the T-atoms.

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dodecasil 3C	melanophlogite
SG = Fd3	SG = Pm3n
a = 19.445(1)Å	a = 13.459(2)Å
136SiO ₂ ·10.1[Xe] ¹² ·5.0[Xe] ¹⁶	46SiO ₂ ·1.0[Xe] ¹² ·3.7[Xe] ¹⁴
R = 7.4%; R _w = 5.4%; (3σ)	R = 8.4%; R _w = 5.4%; (3.5σ)

Tab.: Results of the structure refinement

As already observed for clathrasils with organic guest species the compounds under investigation also showed unusually high displacement parameters for the O-atoms of the silica framework (Liebau, F.: "Structural chemistry of silicates", Springer, Berlin, 1985, p. 22). As a consequence, average d(Si-O) (1.57Å) is too short and \angle (Si-O-Si) (172°) is too large. Electron density maps of the O-atoms, however, clearly resolved distinct split maxima indicating positional disorder (Fig.). Refinement of the split atom model for the O-atoms improved significantly the statistics with angles and distances in the range expected (d(SiO) = 1.59Å; \angle (Si-O-Si) = 162°).

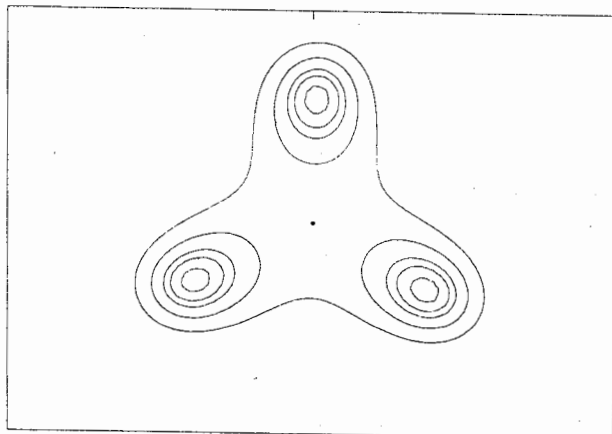


Fig.: Split maxima in the electron density distribution of O(4) in dodecasil 3C viewed along [111]

PS-08.02.10 STUDIES OF ELECTRON DENSITY AND STRUCTURAL PROPERTIES OF SOME SPHERO-HYDRIDO-SILSESQUIOXANES. By Karl Wilhelm Törnroos^{*}, Hans-Beat Bürgi^a, Finn Krebs Larsen^b, Gion Calzaferri^c and Bernard Delley^d.

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Sphero-silsesquioxanes are cage-like molecules composed of several RSiO_{1.5} units. The substituent, R, may vary but is in the present case hydrogen. The sphero-silsesquioxanes have been subject to extensive investigations as to synthesis procedures, physical and chemical properties and technical applications. This report explores their structural properties.

The hydrogen substituted species exhibit chemical instability in that they are oxygen and moisture sensitive, as well as being intrinsically

unstable due to intermolecular nucleophilic attacks. Their intriguing structural properties stem to a large extent from the combination of flexible Si-O-Si angles and non-flexible O-Si-O angles in the molecules. Analysis of displacement parameters has successfully been applied to characterise these properties. The molecules also represent lucid examples of the well-known geometric relation between the Si-O-Si angle and the Si-O bond distance.

The smaller representative, H₈Si₈O₁₂, (HT)₈ forms high quality crystals, has relatively high molecular symmetry, and is thus quite suitable for an accurate study of its electron density distribution by diffraction methods. Although the site symmetry in the crystal is $\bar{3}$, (C_{3i}), the molecular symmetry is close to $m\bar{3}$, (T_h), (within two e.s.d.'s in terms of distances). This is conveniently put to use in the multipole parameterization. The chemical instability of the compound represents a challenge as well as an experimental and computational difficulty. X-ray data have been collected at room temperature, at 100 K and at 9.5 K. The study of the electron density distribution has also been supplemented with a 30 K single crystal neutron measurement (Törnroos, K.W., to be published), and with theoretical calculations of the electron density, applying local-density-functional methods (Törnroos, K.W., Schwarzenbach, D., Larsen, F.K. and Delley, B., to be published). An explanation for the lowering of the (HT)₈ ideal molecular symmetry in the crystalline state, O_h → $\bar{3}$, has been given based on analysis of the significant deviations from rigid body behaviour (Auf der Heyde, T.P., Bürgi, H.-B., Bürgi, H. and Törnroos, K.W. (1991). CHIMIA, 45, 38-40). Results on the electron density deformation study of (HT)₈ are presented.

The two larger molecules investigated, H₁₀Si₁₀O₁₅, (HT)₁₀ and H₁₂Si₁₂O₁₈, (HT)₁₂ are not suited for electron density work, but their structures show interesting features, concerning mainly effects of internal molecular vibrations and their implications on the lowering of the molecular symmetry, in the case of (HT)₁₀, D_{5h} → C₂. This particular problem has been assessed by Principal Component Analysis. Comparisons with (CH₃T)₁₀, show that the distortions on the molecular framework do not depend of the type of substituent. The findings on these effects are presented for the (HT)₁₀ molecule. It is planned to study both the electron density and geometrical properties of silsesquioxane molecules with different types of substituents, e.g. halogens.

PS-08.02.11 SINGLE CRYSTAL STRUCTURE ANALYSIS OF NONASIL(PYR), 88SiO₂·4C₄H₉N. By B.Marler^{*}, H.Gies Institut für Mineralogie, Ruhr-Universität Bochum, Germany.

Nonasils belong to the clathrasils, a distinct class of porous tectosilicates. Clathrasils are clathrate compounds with a 3-dimensional 4-connected host framework of silica possessing cage-like voids which are occupied by (mostly organic) guest molecules.

So far, only very small and intergrown crystals of nonasil had been available limiting the structure analysis to the general determination of the framework topology (B. Marler et al., Journal of Inclusion Phenomena, 1984, 4, 339-349). The framework structure, then, was described in space group Fm $\bar{3}$ m which is the highest possible symmetry of the framework. However, the presence of weak "forbidden" reflexions indicated that the space group symmetry Fm $\bar{3}$ m reflects only an average structure.

Now "large" crystals (120x120x230 μm) of nonasil were grown