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We will demonstrate ways in which structural information on zeolites can be obtained from high resolution images and electron diffraction patterns. Quantitative agreement is obtained between experimental electron diffraction intensities and theoretical calculations. Under favorable circumstances, the weak-phase object approximation (WPOA) can be used to simplify image interpretation and quantification, leading to the determination of the secondary building units (SBUs) of the framework.

**MS-06.02.05** ([CH₃NH₄]₂Sb₂S₅), AND Cs₄Sb₄S₁₀(0,O,S); TWO ZEOLITE-LIKE PHASES WITH NANOPOROUS SULFOANTIMONATE(III) FRAMEWORKS. By F. Liebau and X. Wang, Mineralogisches Institut der Universität Kid, Germany.

In the course of a systematic search for nanoporous materials with non-tetrahedral host frameworks, we synthesized single crystals of the two title compounds and determined their structures from X-ray diffraction data.

**[CH₃NH₄]₂Sb₂S₅;** triclinic red plates; $a = 15.866(3)$ Å, $b = 11.58(2)$ Å, $c = 8.295(2)$ Å, $\alpha = 71.46(2)^\circ$, $\beta = 75.71(2)^\circ$, $\gamma = 82.25(2)^\circ$, $Z = 2$, space group $P1$. $R = 0.061$, $R_w = 0.052$ for 3172 independent reflections with $I > 3\sigma(I)$ and 215 variables.

**Cs₄Sb₄S₁₀(O,S);** triclinic red needles; $a = 11.872(12)$ Å, $b = 13.277(5)$ Å, $c = 14.859(9)$ Å, $\alpha = 85.58(5)^\circ$, $\beta = 85.32(5)^\circ$, $\gamma = 86.19(4)^\circ$, $Z = 2$. Reflections with $h = 2n + 1$ are weak but sharp. An average structure with $u = n/2$ was refined to $R = 0.061$, $R_w = 0.052$, $\mu$ / $\mu$ using 1136 independent reflections with $I > 2.5\sigma(I)$ and 92 variables.

Both structures contain [Sb₅S₆] pyramids with d(Sb-S) = 2.65 Å, most of which are complemented by one or two S atoms with d(Sb-S) between 2.85 Å and 3.3 Å to form [Sb₅S₆] octahedra with n = 4, 5, i.e. distorted octahedra with (6-n) ligands missing. In each of the two structures these 5-octahedra share edges and/or corners via common S atoms to form a 3-dimensional framework. The large cations are located in channel-like pores of the respective frameworks (Fig. 1).

Support from the DFG is gratefully acknowledged.

**MS-06.02.06** THE STRUCTURE OF A NEW COBALT CONTAINING ALUMINO-PHOSPHATE. By Przisl Filipczak, Lubo Kopefd, Department of Chemistry and Chemical Technology, University of Ljubljana, Slovenia, and Natasja Zabokrtsk, National Institute of Chemistry, Ljubljana, Slovenia, and Department of Chemistry and Chemical Technology, Ljubljana, Slovenia.

**SUMMARY.** The novel structure has been determined by using a single crystal of CoAlPO₄ and CO₃N₃ to collect data with MoKa radiation on an Enraf-Nonius CAD-4 diffractometer. The space group is $P2_1_2_1_2_1$. The structure contains distorted octahedral coordination of cobalt atoms and two PO₄ tetrahedral building blocks. The presence of template molecules ethyldiaminediitride has been determined. The cobalt atoms are coordinated to five framework oxygen atoms and one nitrogen $\text{n}^\text{1}$ of the ethylene-diamine.

**INTRODUCTION.** The structure determination of the discussed AIPO₄-based material was undertaken as part of our studies of aluminophosphates, where aluminium and phosphorus are replaced by small amounts of other elements, mainly transition metals. The substitution of a new group of microporous materials, which indicate to be useful for catalytic and adsorption applications and many studies of CoAPO-molecular sieves have been reported recently, with respect to stability. Redox behavior and associated acidic properties (Krauss-Czerniak et al.) octahedral coordination of the cobalt atom in such compounds is rare, in spite of the hot, that for Co$^{II}$ ion, as well as for several other ions of the first transition series, ligand-field stabilization energies disfavor the tetrahedral configuration relative to the octahedral one. From some points of view it is consistent, since the available data (Krauss-Czerniak et al.) show, that the occurrence of Brønsted acidic properties is related to the presence of tetrahedral MeO₄Co$^{II}$ units.

**EXPERIMENTS.** The synthesis of a new compound has been performed using the reaction gel of molar composition 0.4 Co(Al): 0.8 Al₂O₃ : 1.0 P₂O₅ : 1.0 en : 50 H₂O (en = ethylenediamine, en = acetic), following the procedure of crystallization described by Wilson & Plating. In a closed-lined autoclave under static conditions at 460 K over 4 days, pink needle-shaped prismatic crystals were obtained. A crystal of 1.14 x 0.34 x 0.25 mm in size was used for data collection. The crystal structure was solved by direct methods. An absorption correction was made using Gaussian method (g = 2.217 mm$^{-1}$). Nonhydrogen atoms were refined anisotropically and hydrogen atoms, identified in an electron density map, isotropically. The final $R$ (on $F$) was 0.037, $R_w$ = 0.029 for 2326 contributing reflections and 182 parameters.
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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 7.3° and indicates a relatively high distortion of the octahedron. The Al - O distances in the coordination tetrahedra are in the range of 1.278(1) Å to 1.709(1) Å and the bond angles from 107.7(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 ethyleneimine molecule is in a protonated form to compensate the negatively charged framework. One nitrogen atom N(3) 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.


MS-08.02.07 STRUCTURE AND PHASE TRANSITION OF ORTHOHOMBIC AIPO4-5. By N. Ohrishi*, T. Kajtani, O. Terasaki, S. Quin* 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 AIPO4-5 is one in a new family of crystalline, microporous aluminophosphate molecular sieves. The AIPO4-5 phases can be synthesized with various kinds of structure directing agents (templates), and they all show the same hexagonal structure. Recently, we synthesized a new type phase similar to the AIPO4-5 using a synthesis medium containing fluoride anions and tripropylamine 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 AIPO4-5, but has an orthorhombic unit cell with space group symmetry Cc2 and lattice parameters of a = 13.78 Å, b = 23.33 Å and c = 8.44 Å. 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 CLATHRASILS DODECASI. 3C AND MELANOPOHITOGITE by B. Marler*, S. Ohmann, H. Gies Inst. f. Mineralogie, Ruhr-Universität Bochum, 46300 Bochum, Germany

Clathrasils are host-guest compounds with host composition Si2O7 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 Si2O7 framework requires the presence of the guest molecules during synthesis where they act as templates. In the clathrasil dodecasil 3C, 136 SiO2·91M12·3M16, and melanohiphite, 46SiO2·89M12·4M14, the Xe-atoms occupy 12-hedral (M12), 14-hedral (M14), and 16-hedral (M16) cage-like voids with occupancies m, n, p, and q. Whereas Xe fills tightly the 12-hedral in dodecasil 3C and melanohiphite, 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^, C.A. Fyfe^, H. Gies^, D.E. Cox^, T. Y. Feng^, B. Marler^

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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 considerably 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 complementary technique to x-ray diffraction. The 29Si 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 anionic environment of the T-atoms, and are very sensitive to any change due to defect, temperature of 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.

3D 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 symmetry and how these effects influence the local geometry of the T-atoms.