

08-Inorganic and Mineralogical Crystallography

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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 (SBU) of the framework.

MS-08.02.05 $[\text{CH}_3\text{NH}_3]_2\text{Sb}_8\text{S}_{13}$ AND $\text{Cs}_4\text{Sb}_{14}\text{S}_{20}(\text{O},\text{S})_3$: TWO ZEOLITE-LIKE PHASES WITH NANOPOROUS SULFOANTIMONATE(III) FRAMEWORKS. By F. Liebau* and X. Wang, Mineralogisches Institut der Universität Kiel, 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.

$[\text{CH}_3\text{NH}_3]_2\text{Sb}_8\text{S}_{13}$: triclinic red plates; $a=15.866(3)\text{\AA}$, $b=11.581(2)\text{\AA}$, $c=8.295(2)\text{\AA}$, $\alpha=71.46(2)^\circ$, $\beta=75.71(2)^\circ$, $\gamma=82.25(2)^\circ$, $Z=2$, space group $P\bar{1}$. $R=0.061$, $R_w=0.052$ for 3172 independent reflexions with $I > 3\sigma(I)$ and 215 variables.

$\text{Cs}_4\text{Sb}_{14}\text{S}_{20}(\text{O},\text{S})_3$: triclinic red needles; $a=11.872(12)\text{\AA}$, $b=13.277(5)\text{\AA}$, $c=14.859(9)\text{\AA}$, $\alpha=84.58(5)^\circ$, $\beta=85.52(5)^\circ$, $\gamma=86.19(4)^\circ$, $Z=2$. Reflexions with $h=2n+1$ are weak but sharp. An average structure with $a'=a/2$ was refined to $R=0.061$, $R_w=0.052$ in $P\bar{1}$ using 1136 independent reflexions with $I > 2.5\sigma(I)$ and 92 variables.

Both structures contain $[\text{SbS}_3]$ pyramids with $d(\text{Sb-S}) \leq 2.65\text{\AA}$, most of which are complemented by one or two S atoms with $d(\text{Sb-S})$ between 2.85\text{\AA} and 3.3\text{\AA} to form ψ - $[\text{SbS}_n]$ octahedra with $n=4, 5$, i.e. distorted octahedra with (6-n) ligands missing. In each of the two structures these ψ -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.

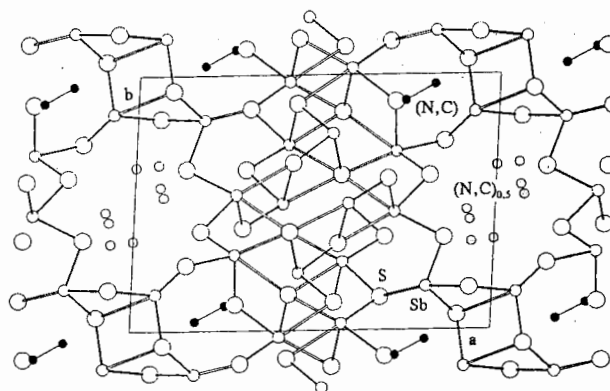


Fig.1 Projection of the structure of $[\text{CH}_3\text{NH}_3]_2\text{Sb}_8\text{S}_{13}$ along $[001]$. Open bonds: 2.85-3.3\text{\AA}, Solid bonds: 2.39-2.65\text{\AA}.

MS-08.02.06 THE STRUCTURE OF A NEW COBALT CONTAINING ALUMINOPHOSPHATE. By Primož Fajdiga, Ljubo Golič, Department of Chemistry and Chemical Technology, University of Ljubljana, Slovenia, Nataša Zabukovec, National Institute of Chemistry, Ljubljana, Slovenia, Venčeslav Kaučič*, National Institute of Chemistry, Ljubljana and Department of Chemistry and Chemical Technology, Ljubljana, Slovenia.

SUMMARY. The novel structure has been determined by using a single crystal of $\text{CoAlP}_2\text{O}_8\text{C}_2\text{H}_9\text{N}_2$ to collect data with $\text{MoK}\alpha$ radiation on an Enraf-Nonius CAD4 diffractometer. From the method of preparation (Wilson&Flanigen) the AlPO_4 -21 type was expected. The monoclinic unit cell has the following parameters: $a = 8.539(1)\text{\AA}$, $b = 15.540(1)\text{\AA}$, $c = 7.736(1)\text{\AA}$, $\beta = 110.65(1)^\circ$. The space group is $P2_1/c$. Determination of the structure shows distorted octahedral coordination of cobalt atom, and one AlO_4 - and two PO_4 -tetrahedra building the framework. The presence of template molecule ethylenediamine has also been determined. The cobalt atom is coordinated to five framework oxygen atoms and one nitrogen atom of the ethylenediamine.

INTRODUCTION. The structure determination of the discussed AlPO_4 -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 gives a new group of microporous materials, which indicate to be useful for catalytic and absorption applications and many studies of CoAPO -molecular sieves have been reported recently, with respect to stability, redox behavior and associated acid properties (Krausheer-Czarnetski et al.). Octahedral coordination of the cobalt atom in such compounds is rare, in spite of the fact, that for Co^{d7} ion, as well as for several other ions of the first transition series, ligand-field stabilization energies disfavour the tetrahedral configuration relative to the octahedral one. From some points of view it is convenient, since the available data (Krausheer-Czarnetski et al.) show, that the occurrence of Brønsted acidic properties is related to the presence of tetrahedral $\text{MeO}_4/2^-$ units.

EXPERIMENTAL. The synthesis of a new compound has been performed using the reaction gel of molar composition $0.4 \text{Co}(\text{ac})_2 : 0.8 \text{Al}_2\text{O}_3 : 1.0 \text{P}_2\text{O}_5 : 1.0 \text{en} : 50 \text{H}_2\text{O}$ (en = ethylenediamine, ac = acetate), following the procedure of crystallisation described by Wilson&Flanigen. In a teflon-lined autoclave under static conditions at 468 K over 4 days, purple needle-shaped prismatic crystals were obtained. A crystal of $1.14 \times 0.34 \times 0.25 \text{ mm}$ in size was used for data collection. The crystal structure was solved by direct methods. An absorption correction was made using Gaussian method ($\mu = 2.217 \text{ mm}^{-1}$). 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.

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 AlPO₄-5. 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 AlPO₄-5 is one in a new family of crystalline, microporous aluminophosphate molecular sieves. The AlPO₄-5 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 AlPO₄-5 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 AlPO₄-5, but has an orthorhombic unit cell with space group symmetry Ccc2 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 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 SiO₂ 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 SiO₂ framework requires the presence of the guest molecules during synthesis where they act as templates.

In the clathrasils dodecasil 3C, 136 SiO₂*nM¹²*mM¹⁶, and melanophlogite, 46SiO₂*pM¹²*qM¹⁴, 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 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 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 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.