formutual nets superposition. We have used the unique set of programms - Crystal Chemistry Analysis of Structure Similarity by Plane Atomic Nets (CCASS-PAN: Bliznyuk N. A., Borisov S. V., Zh. Strukt. Khim, 33, N. 2, 284-304 (1992)). The type of a cation matrix is defined as a set of layers with certain atomic nets which are interrelated in a given way. As an example let us consider a small group of crystal structures U_2F_9, CsU_2F_9, $BaZrF_{10} \cdot 2H_2O$, $TlBF_4$, $TlZrF_5$, et. al. in which are presented nets of cations 3^2434 (1 rhomb+1 square per unit cell). An ideal example is the cubic structure of U_2F_9 in which cation nets 3^2434 are available in 3 orientations: (002), (020), (200). There are two more close-packed crystallographic layers (112) and (002) for the given structure type. Another group of crystal structures with cation nets $3^34^2+3^6$ (2 rhombs, 1 square per unit cell) may be attributed to the structure type β-K_2UF_6. The high symmetry structure has the ideal type of the net $3^34^2+3^6$ in the (110) layer. Thus it was selected as the standard for a calculation of a similarity measure of the cation arrangement in the structures of Rb_2UF_6, KYb_2F_7, K_2GdF_5, $BaTm_2F_8$, K_5ThF_9 et al. with the same nets. There is a rich variety of crystal structures with cation nets 3^6 combining in the " fluorite-like" type. The consideration of fluoride structure types allows to conclude that a set of close-packed layers is more conservative to a composition change and a loss of some symmetry elements. This work was supported by a grant of Soros fond.

08.02 – The Crystallography of Zeolites and Other Porous Materials

MS-08.02.01

IN SITU STUDIES OF DEHYDRATION PROCESSES IN ZEOLITES USING POWDER DIFFRACTION. By K. Ståhl, Inorganic Chemistry 2, University of Lund, Sweden.

Diffraction studies of dehydration processes of zeolites have given valuable insight in the chemistry of zeolites and may provide important clues to the syntheses and applications of these materials. The so far studied zeolites have shown a variety of dehydration behaviours, involving phase transitions, order/disorder transitions before the final breakdown of the crystal structure. The standard method for structural studies has been to heat a powdered or single crystal sample to a given temperature, seal it off and cool it to room temperature before data collection. Obviously this method will give information from a limited set of dehydration temperatures only, and the results may to some extent be obscured by the cooling to room temperature. Preferably one would like to repeatedly collect complete data sets while the samples are slowly heated up.

With the combination of a position sensitive detector (CPS120 by INEL) and a synchrotron X-ray source (X7B, NSLS, USA), the data acquisition time for zeolite powder diffraction pattern, suitable for Rietveld analysis, can be brought down to the order of minutes. Complete powder diffraction data sets collected every five minutes during intermittent (5 K/step) heating have with this method given detailed information of the dehydration processes in a set of natural zeolites. The nature of the water expulsion, gradual or almost instantaneous, stability limits of cation coordination numbers, and the crystal structures immediately below and above phase transitions are some of the directly obtainable results. Details of the water and sometimes cation diffusion can be extracted. The method itself and the results will be discussed and, where available, compared to data obtained with the standard, fixed dehydration temperature, method.

MS-08.02.02

EVALUATION OF ZEOLITE FRAMEWORKS WITH THE VIEW TO CLASSIFICATION, ENUMERATION AND SOLUTION OF STRUCTURES

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An overview of the current range of zeolite frameworks is presented as defined by their systematic relationships derived from their classification in terms of constituent 3-connected sheets. The application of the various methods for the classification and enumeration of zeolite frameworks and their usefulness in structure classification and solution is considered. Novel sets of hypothetical frameworks are evaluated, including a series for which the channel characteristics are pre-defined in two-dimensions.

MS-08.02.03 RECENT ADVANCES IN THE STRUCTURAL CRYSTALLOGRAPHY AND CRYSTAL CHEMISTRY OF NATURAL ZEOLITES. By G. Artioli, Dipartimento di Scienze della Terra, Università di Milano, Italy.

The number of known natural zeolite mineralssteadily increased in recent years. Several new mineral species are natural analogues of known synthetic phases (bellbergite [BEA], paliasapaite [RHO], tiptopite [CAN], tschernichite [BEA]), and other natural species show novel framework topologies (boggsite [BOG], maricopaite, montesommaite [MON], tvedalite).

The crystal structure of the new minerals will be described, together with the recent advances in the structure analysis and modelling in other zeolite groups: the crystal structure of garronite [GIS] has been determined, perlialite [LTL] was shown to have the zeolite-L framework topology, dachiardite [DAC] shows coexisting domains having different frameworks, and the study of the fully hydrated structure of laumontite [LAU] allows interpretation of the leonhardite-laumontite reversible transformation.

Several other zeolite structures were also recently studied in detail and partly revised: lovdarite [LOV], roggianite [ROG], tugtupite [SOD], gonnardite [NAT]. The presence of tetrahedrally coordinated beryllium in natural zeolitic minerals, and the stability of interrupted framework structures are to be considered common features in zeolites. Natural (chiavennite [CHI], partheite [PAR], roggianite [ROG], wenkite [WEN]) and synthetic (cloverite [CLO]) interrupted framework structures will be described.

MS-08.02.04 QUANTITATIVE IMAGING AND DIFFRACTION OF ZEOLITES USING A SLOW-SCAN CCD CAMERA. By M. Pan* and P.A. Crozier, Center for Solid State Science, Arizona State University, USA.

Zeolites are an important class of low-density aluminosilicate framework structures with applications to the field of catalysis, electronic materials and molecular sieves (D.W. Breck, Zeolite Molecular Sieves, John Wiley & Sons, New York 1974). Structural determination is usually carried out by x-ray diffraction. Unfortunately, it fails partially or completely if the synthesized zeolite crystals have a small grain size (e.g. <1 μm) or the structure contains defects. In this case, high resolution electron microscopy (HREM) and electron diffraction can be powerful techniques to help solve the structures (J.M. Newsam, et al., Proc. R. Soc. Lond. A420 (1988) 375). Zeolites undergo rapid structural damage when exposed to electron irradiation because of the low-density and open framework structures. Hence it is necessary to employ low-dose techniques to perform high resolution structure imaging of zeolites.

Recently, the technology in solid state electronic devices has led to the development of commercially available slow-scan CCD (charge-coupled device) cameras for electron microscopy (P.E. Mooney, et al., Proc. XIIth Congr. for Elec. Microsc., Seattle, WA, Vol. 1 (1990) 164). The main advantages of such a device include linear response, large dynamic range (4×10^3), high sensitivity and digital data storage. All of these are suited to acquiring image and diffraction data from radiation sensitive materials.

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 $[CH_3NH_3]_2Sb_8S_{13}$ AND $Cs_4Sb_{14}S_{20}(O,S)_3$: 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.

$[CH_3NH_3]_2Sb_8S_{13}$: triclinic red plates; a=15.866(3)Å, b=11.581(2)Å, c=8.295(2)Å, α=71.46(2)°, ß=75.71(2)°, γ=82.25(2)°, 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.

$Cs_4Sb_{14}S_{20}(O,S)_3$: triclinic red needles; a=11.872(12)Å, b=13.277(5)Å, c=14.859(9)Å, α=84.58(5)°, ß=85.52(5)°, γ= 86.19(4)°, 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 $[SbS_3]$ pyramids with d(Sb-S)≤2.65Å, most of which are complemented by one or two S atoms with d(Sb-S) between 2.85Å and 3.3Å to form ψ-$[SbS_n]$ 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.

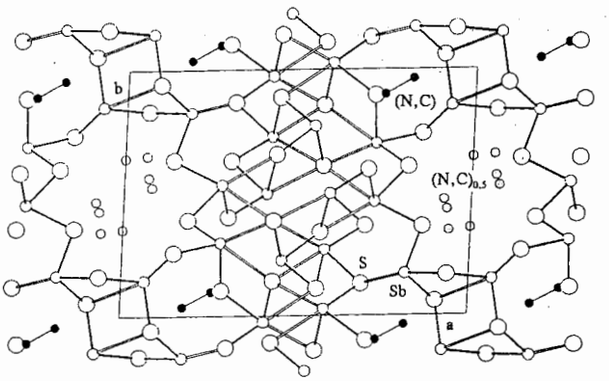

Fig.1 Projection of the structure of $[CH_3NH_3]_2Sb_8S_{13}$ along [001]. Open bonds:2.85-3.3Å, Solid bonds:2.39-2.65Å.

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 $CoAlP_2O_8C_2H_9N_2$ to collect data with MoKα radiation on an Enraf-Nonius CAD4 diffractometer. From the method of preparation (Wilson&Flanigen) the AlPO-21 type was expected. The monoclinic unit cell has the following parameters: a = 8.539(1)Å, b = 15.540(1)Å, c = 7.736(1)Å, β = 110.65(1)°. 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 acidis properties (Krausheer-Czarnetski et al.). Octahedral coordination of the cobalt atom in such compounds is rare, in spite of the fact, that for Co d^7 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 Brönsted acidic properties is related to the presence of tetrahedral $MeO_{4/2}^{2-}$ units.

EXPERIMENTAL. The synthesis of a new compound has been performed using the reaction gel of molar composition 0.4 $Co(ac)_2$: 0.8 Al_2O_3 : 1.0 P_2O_5 : 1.0 en : 50 H_2O (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 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 (μ = 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, Rw = 0.029 for 2326 contributing reflections and 182 parameters.