

PS10.10.09 A UNIVERSAL STRUCTURE-BASED CLASSIFICATION OF INORGANIC MICROPOROUS MATERIALS. F. Liebau, Mineralogisches Institut der Universität Kiel, D-24098 Kiel, Germany

For zeolites and zeolite-like microporous materials, without regard of the type of coordination polyhedra, (tetrahedra octahedra, pyramids etc.) forming their hosts, a systematic classification is proposed. The classification is based on the structure and chemistry of their hosts, h , and the structure of their pores, p , and, in addition, to structure and chemistry of their guest species, g .

Primary classification parameters are:

$CN_{(ceH)}$: coordination number of the central atom, ceH , of the polyhedra (primary building units) from which the host is built by sharing common peripheral atoms, peH .

${}_hD$: dimensionality of the host,

${}_pD$: dimensionality of the pores,

ceH, peH : chemical character of the central and peripheral host atoms,

z : atomic ratio $\Sigma n({}_peH) / \Sigma n({}_ceH)$.

Further subdivision can be made with regard to: (i) host structure by use of fundamental building units (fundamental chains, rings or composite polyhedra), and (ii) pore structure by use of pore width (measured in ring periodicity, P_r , or in Å).

Following this scheme, each inorganic microporous material can be characterized by a Five Parameter Key:

	$CN_{(ceH)}$	${}_hD$	${}_pD$	$ceH ; peH$	z
e.g. clathrasils	4	3	0	Si ; O	2
APOs	4, 5, 6	2, 3	$\leq {}_hD$	Al, P ; O	2
synth. $CsAg_5Te_3$	4,7	3	1	$Te^{2-} ; Ag^+$	1.67

PS10.10.10 STABILITY OF SPATIAL DISTRIBUTION OF WATER MOLECULES IN NATURAL ZEOLITES. Nikolay K. Moroz, Institute of Inorganic Chemistry, Siberian Branch Russian Academy of Sciences, 630090 Novosibirsk, Russia

Proton NMR study of great variety of natural heulandites and clinoptilolites reveals that the water environment in these isomorphous aluminosilicates remains virtually unchanged under variations of the Al/Si ratio and composition of extra cations. In the case of cation-exchanged forms of these crystals the situation is exactly the opposite: as a rule, ion-exchange leads to a drastic rearrangement of water molecules in the framework cavities. Certain distinctions between the water environments in hydrothermal crystals and in zeolitic tuffs have been found.

All NMR measurements and spectra analysis were performed on a portable automatic NMR analyser specially designed for proton NMR studies of hydrogen-containing minerals. The water environments have been characterised via the spatial distributions of proton-proton (p-p) vectors which are determined by the populations of structural positions of water in a crystal and by orientational disordering of molecules in each position. As measures of this distribution, the averaged over lattice values of squares of p-p vector direction cosines were used. These values are easily obtained from NMR line shape analysis when fast diffusion of H_2O molecules by direct interchange of sites takes place [1,2].

The most likely reason of stability of the spatial distribution of water molecules in differ heulandites and clinoptilolites is the H_2O-H_2O dipolar interaction. The energy of this interaction can be minimized in natural zeolites at stage of mineral formation by

appropriate arrangement of extra cations, the Al and Si atoms, and possible by some deformations of framework. The energy minima are not achieved in artificial cation-exchanged forms, because in this case ion-exchange is performed in already formed framework.

References:

1. Ducros P. *Bull. Soc. Fr. Mineral. Cristallogr.* **83**, 85 (1960).

2. Gabuda S.P. and Lundin A.G. *Soviet Physics - JETP* **55**, 1066 (1968).

PS10.10.11 STRUCTURE OF SEMICONDUCTOR CLUSTERS INCORPORATED INTO ZEOLITE X AND SHABASITE. Yu.I.Smolin, Yu.F.Shepelev, A.E.Lapshin and E.A.Vasilyeva, Institute of Silicate Chemistry of Russian Academy of Science, St.-Petersburg, Russia.

The determination of structure of semiconductor clusters incorporated into zeolites using X-ray single crystal diffraction method is discussed. Previously crystal structures of the hydrated and dehydrated forms of Cd and Pb exchanged NaX zeolite were determined. For dehydrated forms data collection was carried out at high temperature. The cycle of crystal structure determinations was carried out on crystals with incorporated CdS clusters, which were obtained by treatment of the zeolite by vapour of H_2S or by repeated exposure of CdX zeolite to the solution of Na_2S with intermediate exchange Na for Cd. Both hydrated and dehydrated forms were investigated. It was shown that CdS clusters occupied positions in supercages of the X-zeolite. The geometry of these clusters are described. We have tried to obtain PbI_2 clusters in X-zeolite by different methods. The satisfactory results were obtained only by treatment of dehydrated form of the NaX zeolite by PbI_2 vapour and by exposure of NaX crystals to supersaturated water solution of PbI_2 . The hydrated and dehydrated forms of X-zeolite with incorporated PbI_2 clusters are described. The crystal structure of shabazite-like zeolite with Se atoms which were injected into crystal from vapour, was determined. The Se atoms form 6-membered rings in the shabazite cages. Crystal data for some compounds:

1. h- PbX_2 Fd3, a=25.15(1), 386 F(hkl), R=0.049, Rw=0.053

2. d- PbX_2 Fd3, a=25.05(1), 189 F(hkl), R=0.048, Rw=0.053

3. h- PbI_2 Fd3, a=25.05(1), 235 F(hkl), R=0.052, Rw=0.060

5. [CdX + CdS] Fd3, a=24.84(1), 715 F(hkl), R=0.057, Rw=0.062

6. Se-shabazite R-3m, a=9.376(3), $\alpha=93.56(5)^\circ$, 182 F(hkl), R=0.075, Rw=0.084.

PS10.10.12 APPLICATIONS OF SYNCHROTRON/IMAGING PLATE SYSTEM TO ELUCIDATE THE STRUCTURE AND SYNTHETIC PATHWAYS TO OPEN FRAMEWORK ANTIMONY SULFIDES. Kemin Tan, John B. Parise and Younghee Ko, Department of Earth and Space Sciences State University of New York at Stony Brook Stony Brook, New York 11794, Alex Darovsky SUNY X3A Beamline, National Synchrotron Lingh Source Brookhaven National Laboratory, Upton, New York 11973, Poul Norby and Jonathan C. Hanson, X7B Beamline, National Synchrotron Lingh Source Brookhaven National Laboratory, Upton, New York 11973.

Open framework antimony sulfides are potential useful optical and catalytic materials. Recrystallization of antimony sulfide in the presence of organic templates under hydrothermal condition has generated a number of novel open framework phases. The single crystal of these materials are usually small and unsuitable for conventional x-ray diffractometry. Further, multiple-phases can crystallize from one batch of a hydrothermal experiment and this can makes it difficult to obtain one pure phase for further studies and applications. In order to determine the systematics of structure for these novel materials, single crystal diffraction data have been collected using the imaging plate (IP) system at the NSLS beamline X-3A. From these data, several structures have been solved and their structural relationships have been analyzed. A $Sb_4S_7^{(2-)}$ single chain has been found to be a major building block in these materials. It is also important to follow the possible crystallization pathways of these phases,

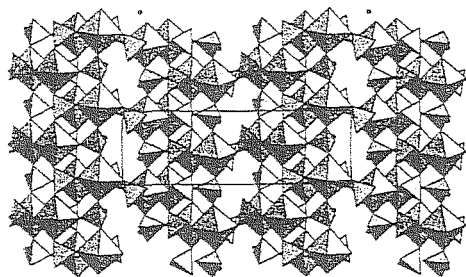
and their dependence on such synthetic parameters as pH, sulfur content, temperature and aging, the transformations from starting materials. We have done this under real-time hydrothermal conditions using powder diffraction and an IP at beamline X7B. From these results, information on the kinetics of formation, useful to optimize future syntheses, has been obtained.

PS10.10.13 THE SYNTHESIS AND CRYSTAL STRUCTURES OF ALKALINE EARTH METAL INDIUM PHOSPHATES. Xuejiao Tang and Abdessadek Lachgar, Chemistry Department, Wake Forest University, Winston-Salem, NC 27109-7486.

Metal phosphates with open framework structures are well known for their adsorptive, catalytic and ion-exchange properties. Al and Ga phosphates have been widely studied and exhibit great structural variations. In contrast, research of In phosphates has been very limited in scope. As a part of our search for open framework metal phosphates, we have recently been investigating ternary alkali or alkaline earth metal indium phosphates using hydrothermal synthesis techniques.

We report the syntheses and crystal structures of alkaline earth metal indium phosphates $A[\text{In}_2(\text{PO}_4)_2(\text{HPO}_4)]$ ($A=\text{Ca}$, Sr or Ba). $\text{Ca}[\text{In}_2(\text{PO}_4)_2(\text{HPO}_4)]$ was synthesized hydrothermally from stoichiometric amounts of CaO and InCl_3 in excess H_3PO_4 and H_2O . The compound crystallizes in monoclinic symmetry, space group $P2_1/n$, $a=6.5708(6)$, $b=20.237(2)$, $c=6.6572(7)\text{\AA}$, $\beta=91.20(1)^\circ$. The structure contains In_2O_{10} dimers built up of two edge-sharing (InO_6) octahedra. The dimers connect to each other through (PO_4 or HPO_4) tetrahedra by sharing all of their oxo ligands. Cations are located in tunnels of 8-member ring opening running along [001] direction. To our knowledge, this is the first reported indium phosphate containing In_2O_{10} dimers.

$\text{Sr}[\text{In}_2(\text{PO}_4)_2(\text{HPO}_4)]$ was obtained hydrothermally from $\text{Sr}(\text{OH})_2$ and InCl_3 (1:1) in excess H_3PO_4 and H_2O . Space group $P2_1/n$, $a=6.615(1)$, $b=20.351(3)$, $c=6.752(1)\text{\AA}$, $\beta=91.00(1)^\circ$. Its structure is analogue to $\text{Ca}[\text{In}_2(\text{PO}_4)_2(\text{HPO}_4)]$



PS10.10.14 ORIENTATION OF NAPHTHALENE IN H-ZSM-5 AS DETERMINED FROM POWDER AND SINGLE CRYSTAL XRAY DATA. H. van Koningsveld and J. C. Jansen, Labs. of Applied Physics and Organic Chemistry and Catalysis, Delft University of Technology, Lorentzweg 1, 2628 CJ Delft, The Netherlands

The adsorption properties of frameworks with the MFI topology (H-ZSM-5 and its Al-free analogue silicalite-1) have received much attention. There is a general agreement that in low-loaded MFI/adsorbent systems the preferred adsorption site is at the intersection of channels.

Recently published papers on the localization of naphthalene (nph) in H-ZSM-5 determined by X-ray Powder Diffraction (hereafter referred to as XPD1 [Mentzen et al.; Zeolites, 13 (1993) 485] and XPD2 [Klein et al.; Microporous Materials, 3 (1994) 291]) show inconsistent results.

In both papers the structure is described in the orthorhombic space group Pnma . In XPD1 as well as in XPD2 the nph molecules (3.8 and 3.0

mols/u.c., respectively) are at the intersection of channels. However, the inversion of the unit cell axes a and b ($a/b < 1$; the empty orthorhombic HZSM-5 framework has $a/b > 1$), as observed in XPD1, is not reported in XPD2. In addition, the orientation of the nph molecules at the intersection of channels in XPD1 and XPD2 is quite different.

We succeeded in preparing a single crystal of the H-ZSM-5 zeolite loaded with 3.68(2) molecules nph per u.c., large enough to allow a single crystal X-ray diffraction study of the material.

The paper describes the structure of the H-ZSM-5/nph complex, gives the ensuing deformation of the channel pores and compares the orientation of nph as determined from powder and single crystal X-ray diffraction. The inversion of the a and b axes is confirmed and the orientation of nph is yet different from the orientations reported in the XPD-papers.

Materials XI Fullerenes

MS10.11.01 DETERMINATION OF THE ENDOHEDRAL NATURE OF THE METALLOFULLERENE $\text{Y}@\text{C}_{82}$ BY MEM. M. Takata, E. Nishibori, B. Umeda, M. Sakata, M. Ohno, H. Shinohara & Y. Saito*, Nagoya University, Nagoya 464-01, Japan, *Mie University, Tsu 514 Japan

The first conclusive evidence of endohedral nature of the Metallofullerene $\text{Y}@\text{C}_{82}$ has been obtained via a Synchrotron X-ray powder diffraction study using the Maximum Entropy Method (MEM). Recently, the synthesis of fullerenes encapsulating various metal atoms within the carbon cage (endohedral metallofullerenes) has stimulated wide interest because of their unusual structural and electronic properties. Observations using STM, EXAFS, HRTEM and ESR have strongly suggested that the metal atoms are indeed inside the fullerene cage. Theoretical calculations also indicate that this is the case. But until now, no structural model has been derived experimentally to confirm the endohedral nature of the metallofullerenes. The $\text{Y}@\text{C}_{82}$ fullerene was separated and isolated by the two-stage high performance liquid chromatography (HPLC) method. The purity of the $\text{Y}@\text{C}_{82}$ fullerene was more than 99.9%. An X-ray powder pattern of $\text{Y}@\text{C}_{82}$ was measured by using Imaging Plate at Photon Factory BL-6A2. The wavelength of incident X-rays is 1.0\AA . The space group is assigned to $P2_1$, monoclinic. The experimental data were analyzed in an iterative way of combination of Rietveld analysis and the MEM. The reliable factor of the obtained MEM charge density is 1.4%. In the MEM charge density, there exist remarkably high densities just inside the C_{82} cage. The number of electrons around the maxima is about 38 which is very close to the atomic number of a yttrium atom. Evidently, the density maxima at the interior of the C_{82} cage is the yttrium atom. The present study revealed the fact that the yttrium atom is displaced from the centre of the C_{82} molecule and is strongly bound to the carbon cage.

MS10.11.02 X-RAY DIFFUSE SCATTERING AND INTER-MOLECULAR INTERACTIONS IN SOLID C_{60} . R. Moret, P. Launois and S. Ravy, Laboratoire de Physique des Solides, URA CNRS 02, Université Paris-Sud, 91405 Orsay, France

Orientalional ordering phenomena control the temperature-pressure phase diagram of solid C_{60} . At present, their understanding is imperfect because microscopic models fail to describe the interactions between the fullerene molecules in details.

Above the $T_0=259\text{K}$ orientational ordering transition the molecules do not rotate freely in the cubic crystal-field and significant short-range orientational correlations are present. They produce radial and azimuthal modulations of the diffuse scattering intensity which have been measured carefully in the first halo ($Q \approx 3.3\text{\AA}^{-1}$) by single crystal X-ray diffraction. Intensity maxima at the special points $X(100)$, $L(1/2, 1/2, 1/2)$ and $\Gamma(000)$ of the Brillouin zone together with some "extra" scattering have been