

**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 <sub>5</sub> Te <sub>3</sub>	4,7	3	1	Te <sup>2-</sup> ; Ag <sup>+</sup>	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<sub>2</sub>O 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<sub>2</sub>O-H<sub>2</sub>O 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<sub>2</sub>S or by repeated exposure of CdX zeolite to the solution of Na<sub>2</sub>S 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<sub>2</sub> clusters in X-zeolite by different methods. The satisfactory results were obtained only by treatment of dehydrated form of the NaX zeolite by PbI<sub>2</sub> vapour and by exposure of NaX crystals to supersaturated water solution of PbI<sub>2</sub>. The hydrated and dehydrated forms of X-zeolite with incorporated PbI<sub>2</sub> 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<sub>2</sub> Fd3, a=25.15(1), 386 F(hkl), R=0.049, Rw=0.053

2. d-PbX<sub>2</sub> Fd3, a=25.05(1), 189 F(hkl), R=0.048, Rw=0.053

3. h-PbI<sub>2</sub> 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<sub>4</sub>S<sub>7</sub>(<sup>2-</sup>) 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,