

by hydrothermal synthesis starting from a reaction mixture of silica, boric acid, water, and pyrrolidine as the template. After heating the mixture at 200°C for two months clear colorless crystals of nonasil(pyr) were obtained. 3595 intensities (Mo K α , $2\theta_{\text{max.}} = 60^\circ$) of a single crystal of nonasil(pyr) were collected using omega scan mode on a Syntex R3 diffractometer ($R_{\text{int}} = 0.031$). 1697 reflexions having $I > 3\sigma$ were used for the refinement procedure with the XLS-system.

The structure refinement ($R = 0.092$, $R_w = 0.068$) revealed that nonasil(pyr) possesses the space group $Cmca$ which is a subgroup of $Fmmm$. 7 symmetrically inequivalent silicon and 14 inequivalent oxygen positions are present in the structure.

[SiO₄]-tetrahedra are corner-linked via common oxygen bridges and form a 3-dimensional silica framework. The framework consists of three different types of cages: the [5⁴6⁴]- and the [4¹5⁸]-cages which are too small to house guest molecules and the [5⁸6¹²]-cages which contain the pyrrolidine molecules.

The silica framework of nonasil(pyr) shows unusually short Si-O distances and high Si-O-Si angles which are associated with unusually large temperature factors of the oxygen atoms. The mean values of $d_{\text{Si-O}}$ and $\angle_{\text{Si-O-Si}}$ (Table 1) differ considerably from those of the dense silica polymorphs ($d_{\text{Si-O}} = 1.608 \text{ \AA}$, $\angle_{\text{Si-O-Si}} = 144^\circ$) but are comparable with the values of other clathrasil structures like

dodecasil 3C	($d_{\text{Si-O}} = 1.566 \text{ \AA}$, $\angle_{\text{Si-O-Si}} = 174.5^\circ$),
dodecasil 1H	($d_{\text{Si-O}} = 1.565 \text{ \AA}$, $\angle_{\text{Si-O-Si}} = 170.4^\circ$),
melanophlogite	($d_{\text{Si-O}} = 1.576 \text{ \AA}$, $\angle_{\text{Si-O-Si}} = 168.8^\circ$).

These unusual values are interpreted as due to static or dynamic disorder (F. Liebau: "Structural Chemistry of Silicates", 1985, Springer Verlag, Berlin, p. 22-30).

Distance or angle	range of values	mean values
$d_{\text{Si-O}}$	1.554(8) - 1.625(9)Å	1.579Å
$\angle_{\text{Si-O-Si}}$	141.9(6) - 171.9(5)°	158.9°

Table 1:
Selected distances and angles of nonasil(pyr).

Difference Fourier syntheses showed that the guest molecules are positionally disordered. Therefore, the guest molecules were simulated by carbon and nitrogen atoms located in six different positions. The coordinates of these positions were obtained from the highest maxima of the difference syntheses.

A detailed analysis of the disorder of the framework atoms and guest molecules is in progress.

PS-08.02.12 HIGH TEMPERATURE X-RAY DIFFRACTION STUDY OF MULLITE FORMATION FROM Al_2O_3/SiO_2 GELS.
By E. Tkalčec(1), B. Gržeta(2) and H. Ivanković(1), (1)Faculty of Chemical Engineering and Technology, University of Zagreb, POB 177, and (2)Ruđer Bošković Institute, POB 1016; 41001 Zagreb, Croatia

Mullite, $3Al_2O_3 \cdot 2SiO_2$, has recently gained an increasing interest as a material for advanced ceramic application. Although the formation of mullite from monophasic and diphasic gels has been intensively investigated recently, there is still a lack of complete understanding and controlling the mullite formation.

Amorphous gels of Al_2O_3/SiO_2 in the molar ratio 3/2 were prepared by slow hydrolysis of tetraethoxysilane and aluminium nitrate 9-hydrate at pH=2 and pH=7. The effect of the preparation routes on the thermal behaviour of the gels were studied using high temperature

in situ XRD measurements and DTA. The gel prepared at pH=2 yielded mainly 2/1 mullite and a small quantity of the spinel phase at T=940°C. On further heating up to 1400°C the 2/1 mullite gradually transforms to the 3/2 mullite. The gel prepared at pH=7 yielded mainly the spinel phase and a small quantity of mullite at T=1000°C. The amount of mullite significantly increased at T=1200°C, this being a consequence of the spinel phase to mullite transformation. The molar ratio of Al_2O_3/SiO_2 of this mullite follows the same temperature dependence as that of the mullite formed from the gel prepared at pH=2.

PS-08.02.13 STRUCTURAL REFINEMENTS OF CATION-EXCHANGED GMELINITES. By M. Sacerdoti*(1), E. Passaglia(2) & R. Carnevali(2). (1)Istituto di Mineralogia, Università di Ferrara, Italy; (2)Istituto di Mineralogia, Università di Modena, Italy.

The prevailing exchangeable cation in the natural gmelinites (hexagonal zeolite) is normally, Na, but also Ca and K. To point out the crystallographic variations induced by the exchangeable cations, three natural samples have been exchanged with Na, K and Ca, and the structures of the corresponding forms have been refined. The crystals before X-ray data collection were tested by electron microprobe analysis in order to ascertain the exchange degrees. The exchanged forms show quite different unit cell dimensions with a and c parameter values inversely correlated with each other.

The structural refinements show that the cell dimensions depend on the type of cation in C1 site, located in the gmelinite cage just outside the double 6-ring. The occupancy of this site by the different exchangeable cations (Na, K, Ca) noticeably modifies the diameters of the 8-ring channel (normal to a) as defined by the following O1-O1 (in c direction) and O3-O3 (in a direction) distances:

	$d(O1-O1)$	$d(O3-O3)$	$d(C1-C1)$
Ca-exchanged	5.76	6.90	3.11 (Å)
Na-exchanged	6.24	6.55	3.56
K-exchanged	6.47	6.18	3.79

The C2 site in the main 12-ring channel parallel to c is partially occupied only in the monovalent cations (Na, K) exchanged forms.

PS-08.02.14

THE ANALYSIS OF THE PATHWAYS FOR SOME MOLECULES IN PENTASIL CHANNELS.

By L. M. Borisanova*, L. A. Zassourskaya, Department of Chemistry, Moscow State University, 119899, Moscow, Russia.

The structure of empty (not filled by van der Waals spheres) space in pentasil ZSM-5 was investigated (L. A. Zassourskaya, L. M. Borisanova, Vestn. Mosk. Univ., Ser. 2, Khim., 1990, 31, N5, 454-457). It was found that particles can move most

08-Inorganic and Mineralogical Crystallography

263

freely through the straight channels, the diameter of which is in the range from 2.64 to 3.30 Å. In this work the calculations, which allow to geometrically estimate the possibility of the location and movement of the molecules of xylene isomers and benzene in straight channels in zeolite ZSM-5 were carried out. We used the scanning method in 3 rotational and 3 translational degrees of freedom. All the distances between the atoms of a molecule and the surrounding atoms of the crystal were calculated for each scanning point and were compared with the normal van der Waals contacts. It was assumed that a molecule may be located in the scanning point if considerably shortened intermolecular contacts are absent. The calculation showed, that any of the considered molecules can be placed in a straight channel. However, only benzene and p-xylene molecules can move through such channel, because the overlapping of their van der Waals spheres with those of the channel atoms is acceptable (less 0.35 Å). The identity of the results obtained for the molecules of benzene and p-xylene indicates that the presence of substituent in para-position does not obstruct the movement of the molecule through the channel. Such calculations permit to estimate the geometry of available space.

PS-08.02.15 EVALUATION OF ZEOLITE FRAMEWORKS WITH THE VIEW TO CLASSIFICATION, ENUMERATION AND SOLUTION OF STRUCTURES.

Duncan Akporiaye

SINTEF-SI, P.O. Box 124 Blindern, N-0314 Oslo, Norway.

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.

08.03 - Minerals, Structure and Properties

PS-08.03.01 CRYSTAL CHEMISTRY OF THE CANCRINITE LIKE MINERALS. By R. K. Rastsvetaeva*, Institute of Crystallography Russian Acad. of Sci., Moscow, Russia.

The structural peculiarities of afghanite, bystrite, liottite and the other minerals of the cancrinite group are investigated. A common system of describing the minerals of the cancrinite group by the letters A, B and C is suggested. The system is based on the arrangement of the six-membered rings around the rotation axes 3 along 2/3, 1/3, z and 1/3, 2/3, z and

the screw axis 6 along 0, 0, z of space group $P6_3mc$. The letters correspond to the axes positions. The arrangement of these rings determines the form of the cavities and channels in the structures of this group of minerals. Three types of cavities are found in the structure of cancrinite (AB...), bystrite (ACBC...) and liottite (ACBCBC...). The structure of afghanite (ACACBCBC...) is characterized by combining the minimal cancrinite and maximal liottite cavities. A correlation between the chemical composition and the sizes and forms of the cavities is found.

PS-08.03.02A STUDY ON HOKUTOLITE SYNTHESIS AND ITS CRYSTALLOGRAPHIC ANALYSIS Shu-Cheng Yu* and Jiann-Shing Lee, Department of Earth Sciences, National Cheng-Kung University, Tainan, Taiwan

Hokutolite is a mineral of hot spring deposit and considered to be a solid solution of barite ($BaSO_4$) and anglesite ($PbSO_4$). Natural occurrences of hokutolite reported in literature include Hokuto, Taiwan and Shibukure near Akita Japan. The chemical composition of hokutolite from Taiwan was found to be from 21 mol% $PbSO_4$ to 32 mol% $PbSO_4$.

Synthetic hokutolite samples with different chemical composition were grown in the present study with the starting materials of solutions of $Pb(NO_3)_2$, $Ba(NO_3)_2$ and $(NH_4)_2SO_4$. Two different growth processes were carried out at 95-100°C and ambient pressure conditions, with growth time of 3-4 days.

Optical microscopy and X-ray diffraction analysis suggest that the growth process significantly affects the crystallinity, growth rate and crystal size of the synthetic hokutolite. With two different growth processes, one process produced the sample with 59-71 mol% $PbSO_4$ and the other 73-80 mol% $PbSO_4$, with their corresponding average crystal size being less than 0.5 mm and greater than 0.5 mm, respectively. Extinction anomaly observed in optical microscopy study suggests that the grown materials may exhibit chemical/structural domain in the hokutolite crystal lattice.

PS-08.03.03 THE X-RAY STUDY OF Fe-Ti ORE MINERALS FROM THE PACIFIC OCEAN. By M.T. Dmitrieva, Institute of ore deposits geology, mineralogy, petrology and geochemistry, Russian Acad. Sci., Moscow.

The samples of natural Fe-Ti-oxide minerals from different types of oceanic basalts have been studied by X-ray and electron microprobe analyses. It is estimated that the dominating