

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 $\alpha$ ,  $2\theta_{\text{max.}} = 60^\circ$ ) 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.

[SiO<sub>4</sub>]-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 [5<sup>4</sup>6<sup>4</sup>]- and the [4<sup>1</sup>5<sup>8</sup>]-cages which are too small to house guest molecules and the [5<sup>8</sup>6<sup>12</sup>]-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.**  
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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.**

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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