

08-Inorganic and Mineralogical Crystallography

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dodecasil 3C	melanophlogite
SG = Fd3	SG = Pm3n
a = 19.445(1)Å	a = 13.459(2)Å
136SiO ₂ ·10.1[Xe] ¹² ·5.0[Xe] ¹⁶	46SiO ₂ ·1.0[Xe] ¹² ·3.7[Xe] ¹⁴
R = 7.4%; R _w = 5.4%; (3σ)	R = 8.4%; R _w = 5.4%; (3.5σ)

Tab.: Results of the structure refinement

As already observed for clathrasils with organic guest species the compounds under investigation also showed unusually high displacement parameters for the O-atoms of the silica framework (Liebau, F.: "Structural chemistry of silicates", Springer, Berlin, 1985, p. 22). As a consequence, average d(Si-O) (1.57Å) is too short and $\angle(\text{Si-O-Si})$ (172°) is too large. Electron density maps of the O-atoms, however, clearly resolved distinct split maxima indicating positional disorder (Fig.). Refinement of the split atom model for the O-atoms improved significantly the statistics with angles and distances in the range expected (d(SiO) = 1.59Å; $\angle(\text{Si-O-Si})$ = 162°).

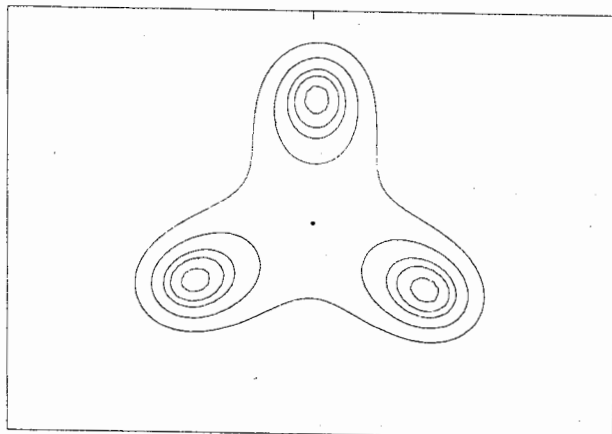


Fig.: Split maxima in the electron density distribution of O(4) in dodecasil 3C viewed along [111]

PS-08.02.10 STUDIES OF ELECTRON DENSITY AND STRUCTURAL PROPERTIES OF SOME SPHERO-HYDRIDO-SILSESQUIOXANES. By Karl Wilhelm Törnroos*, Hans-Beat Bürgi^a, Finn Krebs Larsen^b, Gion Calzaferri^c and Bernard Delley^d.

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Sphero-silsesquioxanes are cage-like molecules composed of several RSiO_{1.5} units. The substituent, R, may vary but is in the present case hydrogen. The sphero-silsesquioxanes have been subject to extensive investigations as to synthesis procedures, physical and chemical properties and technical applications. This report explores their structural properties.

The hydrogen substituted species exhibit chemical instability in that they are oxygen and moisture sensitive, as well as being intrinsically

unstable due to intermolecular nucleophilic attacks. Their intriguing structural properties stem to a large extent from the combination of flexible Si-O-Si angles and non-flexible O-Si-O angles in the molecules. Analysis of displacement parameters has successfully been applied to characterise these properties. The molecules also represent lucid examples of the well-known geometric relation between the Si-O-Si angle and the Si-O bond distance.

The smaller representative, H₈Si₈O₁₂, (HT)₈ forms high quality crystals, has relatively high molecular symmetry, and is thus quite suitable for an accurate study of its electron density distribution by diffraction methods. Although the site symmetry in the crystal is $\bar{3}$, (C_{3i}), the molecular symmetry is close to $m\bar{3}$, (T_h), (within two e.s.d.'s in terms of distances). This is conveniently put to use in the multipole parameterization. The chemical instability of the compound represents a challenge as well as an experimental and computational difficulty. X-ray data have been collected at room temperature, at 100 K and at 9.5 K. The study of the electron density distribution has also been supplemented with a 30 K single crystal neutron measurement (Törnroos, K.W., to be published), and with theoretical calculations of the electron density, applying local-density-functional methods (Törnroos, K.W., Schwarzenbach, D., Larsen, F.K. and Delley, B., to be published). An explanation for the lowering of the (HT)₈ ideal molecular symmetry in the crystalline state, O_h → $\sim T_h$, has been given based on analysis of the significant deviations from rigid body behaviour (Auf der Heyde, T.P., Bürgi, H.-B., Bürgi, H. and Törnroos, K.W. (1991). CHIMIA, 45, 38-40). Results on the electron density deformation study of (HT)₈ are presented.

The two larger molecules investigated, H₁₀Si₁₀O₁₅, (HT)₁₀ and H₁₂Si₁₂O₁₈, (HT)₁₂ are not suited for electron density work, but their structures show interesting features, concerning mainly effects of internal molecular vibrations and their implications on the lowering of the molecular symmetry, in the case of (HT)₁₀, D_{5h} → C₂. This particular problem has been assessed by Principal Component Analysis. Comparisons with (CH₃T)₁₀, show that the distortions on the molecular framework do not depend of the type of substituent. The findings on these effects are presented for the (HT)₁₀ molecule. It is planned to study both the electron density and geometrical properties of silsesquioxane molecules with different types of substituents, e.g. halogens.

PS-08.02.11 SINGLE CRYSTAL STRUCTURE ANALYSIS OF NONASIL(PYR), 88SiO₂·4C₄H₉N. By B.Marler*, H.Gies Institut für Mineralogie, Ruhr-Universität Bochum, Germany.

Nonasils belong to the clathrasils, a distinct class of porous tectosilicates. Clathrasils are clathrate compounds with a 3-dimensional 4-connected host framework of silica possessing cage-like voids which are occupied by (mostly organic) guest molecules.

So far, only very small and intergrown crystals of nonasil had been available limiting the structure analysis to the general determination of the framework topology (B. Marler et al., Journal of Inclusion Phenomena, 1984, 4, 339-349). The framework structure, then, was described in space group Fm $\bar{3}$ m which is the highest possible symmetry of the framework. However, the presence of weak "forbidden" reflexions indicated that the space group symmetry Fm $\bar{3}$ m reflects only an average structure.

Now "large" crystals (120x120x230 μm) of nonasil were grown

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