08-Inorganic and Mineralogical Crystallography

<table>
<thead>
<tr>
<th>dodecasil 3C</th>
<th>melanophlogite</th>
</tr>
</thead>
<tbody>
<tr>
<td>SG = Fd3</td>
<td>SG = Pm3n</td>
</tr>
<tr>
<td>a = 19.445Å</td>
<td>a = 13.4592Å</td>
</tr>
<tr>
<td>13SrO2:10SiO2:12:5:8:18</td>
<td>46SrO2:19:3:8:12:3:7:14</td>
</tr>
<tr>
<td>Rl = 7.4%; Rw = 5.4%; (3G)</td>
<td>Rl = 8.4%; Rw = 5.4%; (3.5G)</td>
</tr>
</tbody>
</table>

Table: Results of the structure refinement

As already observed for clathrasil 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 4(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; 4(Si-O-Si) = 162°).

Fig.: Split maxima in the electron density distribution of O(4) in dodecasil 3C viewed along [1\(\bar{1}1\)]

PS-08.02.10 STUDIES OF ELECTRON DENSITY AND STRUCTURAL PROPERTIES OF SOME SPHÈRO-HYDRODI-SILESQUIXANES. By Karl-Wilhelm Tornroos, Hans-Beat Bürgi, Finn Krebs Larsen, Gion Calafati and Bernard Delley.

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Sphère-silesiquoxanes are cage-like molecules composed of several RsSiO₄ units. The substituents, R, may vary but is in the present case hydrogen. The sphère-silesiquoxanes 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 from 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 characterize these properties. The molecules also represent vivid examples of the well-known geometric relation between the Si-O-Si angle and the Si-O bond distance.

The smaller representative, H₂SiO₄, (HT)₉ 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 six symmetry in the crystal is 3 (C₃ₐ), the molecular symmetry is close to m 3 (T₃ₐ), (within two e.s.d.'s in terms of distances). This is conveniently put to use in the multiple 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 (Tornroos, K.W., to be published), and with theoretical calculations of the electron density, applying local-density-functional methods (Tornroos, K.W., Schäfer, D., Larsen, F.K. and Delley, B. to be published). An explanation for the lowerering of the (HT)₉ molecular symmetry in the crystalline state, O₃ₐ → T₃ₐ, has been given based on analysis of the significant deviations from rigid body behaviour (Auer der Heye, T.P., Bürig, H.-B., Bürig, H. and Tornroos, K.W. 1991). CSDA, 45, 38-40. Results on the electron density deformation study of (HT)₉ are presented.

The two larger molecules investigated, H₁₀SiO₁₂O₁₄, (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. D₉₃ → C₃ₐ. This particular problem has been assessed by Principal Component Analysis. Comparisons with (CH₃)₉₀ 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 silesiquoxane molecules with different types of substituents, e.g. halogen.

PS-08.02.11 SINGLE CRYSTAL STRUCTURE ANALYSIS OF NONASIL(PYR), 8SiO₄:4C₅H₄N. By B. Marler, H. Gies Institut für Mineralogie, Ruhr-Universität Bochum, Germany.

Nonasil belong to the clathrasils, a distinct class of porous zeolites. 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 Fm3m which is the highest possible symmetry of the framework. However, the presence of weak "forbidden" reflections indicated that the space group symmetry Fm3m 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 pyrophyllite as the template. After heating the mixture at 200°C for two months clear colorless crystals of nonaisil(ppy) were obtained. 3595 intensities (Mo Kα, 2θ max. = 60°) of a single crystal of nonaisil(ppy) were collected using omega sapphire crystal on a Syntax R3 diffractometer (Rint = 0.031). 1697 reflections having I>3σ(I) were used for the refinement procedure with the XLS system.

The structure refinement (R = 0.092, Rw = 0.068) revealed that nonaisil(ppy) possesses the space group Cmcn which is a subgroup of Pnma. 7 symmetry inequivalent silicon and 14 inequivalent oxygen positions are present in the structure. [SiO₄]²⁻ 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 [5r⁶f⁶]⁻ and the [4r⁵f⁵]⁻ cages which are too small to hold guest molecules and the [5r⁶f⁶]⁻ cages which contain the pyrophyllite molecules.

The silica framework of nonaisil(ppy) 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 δ⁶-O and δ⁶-O-Si (Table 1) differ considerably from those of the dense silica polymorphs (δ⁶-O = 1.608 A, δ⁶-O-Si = 144°) but are comparable with the values of other clays or silicate structures like

dodacextral 3C
(δ⁶-O = 1.566 A, δ⁶-O-Si = 174.5°),
dodacextral 1H
(δ⁶-O = 1.565 A, δ⁶-O-Si = 170.4°),
melanophlogite
(δ⁶-O = 1.576 A, δ⁶-O-Si = 168.8°).

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 range of values mean or angle values
| 4S-O | 1.554(3) - 1.625(3) | 1.59(2) |
| 4S-O-Si | 141.9(6) - 171.9(5) | 158.9(6) |

Table 1: Selected distances and angles of nonaisil(ppy).

Difference Fourier syntheses showed that the guest molecules are positioned disorderly. 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 AL₂O₃-SiO₂ GELS. By E. Klafic (1), B. Grzeta (2) and H. Ivanovski (1), (1) Faculty of Chemical Engineering and Technology, University of Zagreb, POB 177, and (2) Rudorf Bolkovic Institute, POB 1016, 41000 Zagreb, Croatia.

Mullite, 3Al₂O₃·2SiO₂, has recently gained an increasing interest as a material for advanced ceramic application. Although the formation of mullite from monosilicic and diphasic gels has been intensively investigated recently, there is still a lack of complete understanding and controlling the mullite formation.

Amorphous gels of Al₂O₃·SiO₂ in the molar ratio 3/2 were prepared by slow hydrolysis of tetraethoxysilane and aluminium nitrate 9. Hydrolysate 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 yield mullite 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 Al₂O₃·SiO₂ of the 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 GEMELINES. By M. Saccedro (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 gemelinite (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 microscopy 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 CI site, located in the gemelinite cage just outside the double 6-ring. The occupancy of this site by the different exchangeable cations (Na⁺, K⁺, Ca⁺) noticeably modifies the diameter of the 6-rings channel (normal to a) as defined by the following O1-O1 (in a direction) and O1-O3 (in a direction) distances:

<table>
<thead>
<tr>
<th>d(O1-O1)</th>
<th>d(O3-O3)</th>
<th>d(Cl1-C1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.76</td>
<td>6.24</td>
<td>3.11</td>
</tr>
<tr>
<td>5.65</td>
<td>6.24</td>
<td>3.56</td>
</tr>
<tr>
<td>6.18</td>
<td>6.24</td>
<td>3.79</td>
</tr>
</tbody>
</table>

The CI site in the main 12-rings channel parallel to a 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. Borisova, L. A. Zaslavskaya, Department of Chemistry, Moscow State University, 119992, Moscow, Russia.

The structure of empty (not filled by van der Waals spheres) space in pentasil 25M-S was investigated (L. A. Zaslavskaya, L. M. Borisova, Vestn. Mosc. Univ. Ser. 2, Khim., 1990, 31, N5, 454-457). It was found that particles can move most