

08-Inorganic and Mineralogical Crystallography

261

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°).

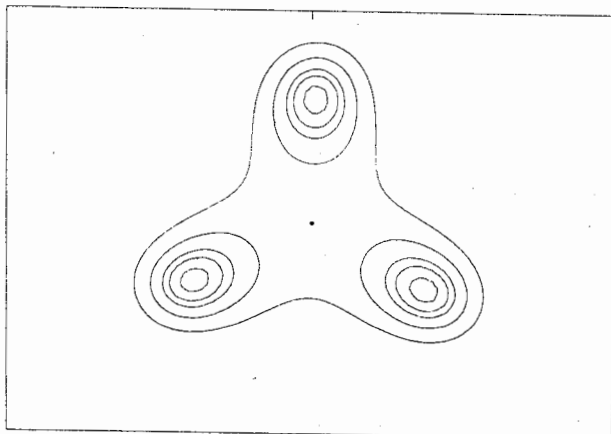


Fig.: Split maxima in the electron density distribution of O(4) in dodecasil 3C viewed along [111]

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