The structure of the low-temperature form of pyrrolidine silica-sodalite (PYS-SOD-LT)

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Silica-sodalites consist of a simple neutral silica framework with cage-like voids (host) and neutral organic molecules (guest), which interact only via weak interactions like van der Waals forces. The chemical composition per unit cell is $Si_{12}O_{24} * 2M$ (M = guest species). Because of their simplicity they are important model compounds to explore host-guest interactions. So far, eight silica-sodalite materials are known containing different organic molecules as guest species [1, 2, 3, 4, 5]. All these as-made materials are cubic at room temperature. Several silica-sodalites, however, undergo phase transitions at lower temperature or higher pressure [e.g. 6, 7].



Fig. 1: The pyrrolidine molecule (C_4H_8N) . Fig.

Fig. 2: The sodalite cage.

Using the "quasi dry synthesis route" cubo-octahedral crystals of PYS-SOD were obtained in the system SiO₂/pyrrolidine/NH₄F/(H₂O) in sealed silica glass tubes at 160°C. Synchrotron powder diffraction data were collected at 171 K at HASYLAB, Hamburg, beamline B2 ($\lambda = 0.49986$ Å). Variable temperature XRD and polarisation microscopy were used to investigate the phase transition.

PYS-SOD undergoes a reversible phase transition at ca. 216 K which is detectable by polarisation microscopy and X-ray diffraction. At low temperature the "crystal" shows optical anisotropy with twin lamellae orientated along <100>. No additional phase transition was detected when lowering the temperature down to 80 K.

The high temperature form, PYS-SOD-HT, is cubic with space group symmetry I-43m (no. 217) and possesses a lattice parameter of $a_0 = 8.8843(2)$ Å at room temperature. NMR spectroscopy and structure analysis proved that at this temperature the pyrrolidine molecule is dynamically disordered (similar to other silica sodalites) with a sphere-like electron density distribution in the cage.

The powder diagramm of the low temperature form, PYS-SOD-LT, recorded at 171 K can unambiguously be indexed in the hexagonal system with lattice parameters of a = 12.6633 Å and c = 7.5674 Å. Reflection conditions indicated a R-centered unit cell with five possible space groups: R3, R3m, R32, R-3m and R-3. "Distance-least squares" refinements were used to discriminate between these space groups showing the best geometrical fit in SG R-3. This space group was subsequently used for the Rietveld refinement which converged to R_F = 5.8, R_{wp} = 18.7, R_{exp}. = 12.4 and $\chi^2 = 2.3$.

The geometrical analysis of the framework of PYS-SOD-LT (see Table 1) gave Si - O distances of ca. 1.60 Å which are typical for pure silica zeolites. The Si - O - Si angles, however, are considerably larger than expected for a relaxed SiO₂ structure (i.e. ca. 144°).

	PYS-SOD-HT (295 K)	PYS-SOD-LT (171 K)
Space group	I-43m (No. 217)	R-3 (No. 217)
Si-O distances [Å]	1.597(1)	1.61(2), 1.58(2), 1.61(2), 1.60(1)
Si-O-Si angle [°]	159.7(1)	166(2), 153(2)
Unit cell volume [Å ³]	700.2 (2)	700.6 (2) (rhombohedral cell)

Table 1: Comparison between high and low temperature form of pyrrolidine silica-sodalite

After refining the silica framework difference Fourier syntheses showed six (symmetrically equivalent) electron density maxima in the cage representing the four carbon atoms and the nitrogen atom of the occluded guest molecule pyrrolidine. The maxima are arranged as a slightly puckered ring with the plane of the ring lying perpendicular to the 3-fold rotation axis (= c-axis) of the structure. The observation of a six-membered ring is interpreted as a static, orientational disorder of the molecule. For the structure refinement the C- and N-Atoms were best simulated by 1 C-site at a position obtained from the difference electron density map.





Fig. 3: Rietveld plot for the structure refinement of the low temperature form of pyrrolidine silica-sodalite.

Fig. 5: The electron density distribution in the cage (perpendicular to [001] at z = 0).

There are some indications (the moderate quality of the Rietveld fit, anisotropic peak broade-ning, the high Si-O-Si angle) that this structure analysis presents only the average structure. The local symmetry of the cage containing the pyrrolidine molecule is probably lower. Attempts to refine the structure of PYS-SOD-LT with a lower symmetry (o'rhombic, mono-clinic), however, failed. ¹H, ¹³C and ²⁹Si NMR spectroscopy at low temperature is in progress.

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