



<b>Experiment title:</b> <b>Structural study of synthetic mordenite: the effect of dye loading</b>	<b>Experiment number:</b> 01-02-609	
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#### **Purpose:**

The aim of this study was a structural characterization of a dye loaded, synthetic mordenite (preferred molecules sites, disorder). Zeolites allow a spatial arrangement and stabilisation of individual atoms, clusters or molecules. These host-guest systems find applications as artificial antenna systems, where incorporated dyes mimic the natural function of chlorophyll in plants, or one-dimensional semiconductors. Different kinds of microcrystalline (< 1µm) synthetic zeolites (zeolite L, zeolite Y, and ZSM-5) have hitherto been used as hosts for this kind of artificial antenna systems [1]. Very little is known about geometrical arrangement of the dyes in these channels, because of (1) the nano size of the used zeolites (0.1 microns), which is too small for single crystal diffraction, and (2) the high symmetry of the channels exhibiting a pseudo twelve fold axis responsible for pronounced disorder of the incorporated dyes. The incorporation of the organic dye molecules is dependent on the aperture of the zeolite channels. The orientation of the molecule in the channel is determined by the shape and size of the dyes and the zeolite channels. Furthermore, the charge distribution on the internal walls of the zeolite channels may influence the orientation of the trapped molecules. The exact position of the chromophores in the zeolite structure may provide better understanding how the antenna systems work and how the energy transfer can be improved. Mordenite, which was self-synthesised in the home-lab, is particularly suitable for the structural analysis of dye-zeolite systems, because the anisotropic shape of the channel cross-section limits disorder of the enclosed molecules. Cationic thionin blue ( $C_{12}H_9N_3S^+$ ) has been used for dye incorporation by ion exchange [2].

#### **Experiment at BM1A**

Two samples were measured:

- 1) Self-synthesised Na-mordenite single crystal ( $Na_6Al_6Si_{42}O_{96} \times H_2O$ )
- 2) Self-synthesised, partially exchanged Thionin-mordenite single crystal ( $Na_x(C_{12}H_9N_3S)_{1-x} Si_{42}O_{96} \times H_2O$ )

Both samples were mounted on glass needles. Data collection was performed in dose mode for both crystals at room temperature with a wavelength of 0.70192 Å using the MAR image plate. Because of beam instability, there was not enough time to measure a full sphere data collection from the Na-mordenite sample, but quality of the data was sufficient for structure determination.

## Results and discussion

Data reduction of both data sets was performed with the program package CrysAlis (Oxford Diffraction), and structure refinement was carried out with ShelX97. Diffuse scattering was observed in the raw data of both samples. Reciprocal space reconstruction showed that diffuse scattering is appears only on  $hkl$  layers with  $l = 2n + 1$

### Sample 1, Na-mordenite:

After determining the common Si, Al framework and the extraframework cations and molecules, peaks remained in the difference Fourier map. These peaks could not be assigned to extraframework occupants because distances to framework oxygen were too short. In addition, the coordinates of these peaks correspond almost exactly to the  $x, y$ -coordinates of the framework atoms but differ in the  $z$ -coordinate. Most obvious are the difference-Fourier peaks originating from the 4-membered rings of tetrahedra shifted  $\frac{1}{2}$  along  $c$ . If the residual peaks in the difference-Fourier map are analyzed in detail counterparts of all framework positions can be found shifted  $\frac{1}{2}$  along  $c$ . Consequently the entire Si, Al framework is repeated but shifted by  $c/2$ . This new kind of framework defect in synthetic mordenite was compared with the structural features of a natural mordenite sample, where the same phenomenon was found. These results have been published in [3].

**Abstract:** "Single crystal X-ray data were collected on a natural fibrous mordenite of composition  $K_{2.99}Ca_{1.85}Na_{1.06}Al_{7.89}Si_{40.15}O_{96} \times 28 H_2O$  and on a platy, self-grown synthetic mordenite of composition  $Na_6Al_6.02Si_{42.02}O_{96} \times 19 H_2O$ . Diffraction data were measured with a point detector using a sealed X-ray tube and an image plate using synchrotron radiation, respectively. Both structures exhibit the same defect features visible in difference-Fourier maps. Domains of the entire  $Cmcm$  framework structure are reproduced by a non-crystallographic (001) mirror plane at  $z = 0$  and  $z = \frac{1}{2}$ . An identical description is a shift of framework domains  $\frac{1}{2}$  along the  $c$  axis. The concentration of this defect domain is 2.7(2) and 3.1(1)% for the natural and synthetic mordenite, respectively. Reproductions of reciprocal layers from synchrotron image-plate data reveal diffuse scattering for  $hkl$  layers with  $l = 2n + 1$ . The diffuseness of these layers is not homogeneous but concentrates in form of halos around selected reflections allowed for  $C$ -centering. Diffuse features in electron diffraction patterns of natural and synthetic mordenite have been described before and were interpreted either as evidence of  $c/2$  faults or intergrowth with different mordenite-related structure-types. We have modeled a (100) defect interface-layer that is modified from the mordenite characteristic puckered sheet of six-membered rings and allows coherent intergrowth of identical structural subunits shifted by  $c/2$ . The defect domains do not influence or obstruct the 12-membered ring-channels characteristic of this zeolite. The major difference in the Si, Al distribution between the two studied mordenite is that the natural crystal has Al strongly enriched in T3 that is part of the 4-membered rings. It is suggested that a synergetic effect between extraframework cations and Si, Al ordering during crystal growth is responsible for Al enrichment in natural mordenite with ca. 2 Ca pfu close to T3."

### Sample 2, Thionin-modified mordenite:

Although the orthorhombic symmetry of mordenite already limits disorder of the enclosed molecules, the structural refinement of thionin-mordenite showed distinct disorder of the organic molecule along axis of the large 12-membered ring channel. Due to the results of the structure refinement, the molecule site is assumed to be slightly inclined in the center of the 12-membered ring channel. To obtain more reliable structural data, the same diffraction experiment is planned to be performed at 120 K, which should reduce the thermal vibration (and therefore disorder) and allow a more accurate localization of the dye molecule.

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- [2] Simoncic, P., and Armbruster, T. (2002) *Zeolite '02*, Book of Abstracts, 336
- [3] Simoncic P., Armbruster T., (2004) *American Mineral.* 89, p 421-431