



	Experiment title: Structural Investigation of ETS-4 Molecular Sieves	Experiment number: 01-01-36
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Report:

ETS (Engelhard Titanium Silicate) represents a new class of zeolite molecular sieves. The ETS-4¹ variety, $\sim \text{Na}_{3.0}(\text{Ti}_{5.0}\text{Si}_{7.4}\text{O}_{12.0})\text{O}_x$, contains small pores of about 3.7 angstrom.

Largely based upon similarities between laboratory powder XRD data, it was suggested^{1,2} that ETS-4 has the same structure of mineral zorite. The zorite structure was solved by Sandomirskii and Belov³ and superposition structure refined in the space group *Cmmm*. Its framework is formed by TiO_6 octahedral chains and SiO_4 tetrahedra and it contains 12- and 8-membered ring channels. The authors interpreted zorite in terms of 'OD structure' and suggested that groups of TiO_6 octahedra connected to four SiO_4 tetrahedra are randomly distributed in the 12-ring channels leading to an highly faulted material.

Recent investigations⁴ have reported that, although laboratory XPD patterns for ETS-4 and zorite are very similar, ²⁹Si solid state MAS-NMR results suggest that the ETS-4 structure is related to that of zorite but is not its synthetic counterpart. A complete structure solution of ETS-4 has not been achieved yet.

The powder diffraction data were collected on an ETS-4 sample synthesised from the $3.5\text{Na}_2\text{O}-1.2\text{TiO}_2-4.48\text{HCl}-4\text{SiO}_2-110\text{H}_2\text{O}$ system^{5,6}. A borosilicate 0.3 capillary was filled with the sample powder, mounted on the goniometer head and axially spun during data collection on the two-axis diffractometer at SNBL - Station B. The detector slits were adjusted to 0.3 x 8.0 mm. Before starting data collection on the ETS-4 sample, a silicon calibration run was performed. The refined value for wavelength and 2θ -zero were 1.10023 Å and 0.0008°, respectively. The ETS-4 diffraction pattern was recorded in the $2\theta = 3-75^\circ$, using a step of 0.01° and different sampling time on background and peaks, for a total duration of about 22 hours. After measurement data were normalised and averaged using software available at SNBL (ESRFTOSRS and PODSUM⁷).

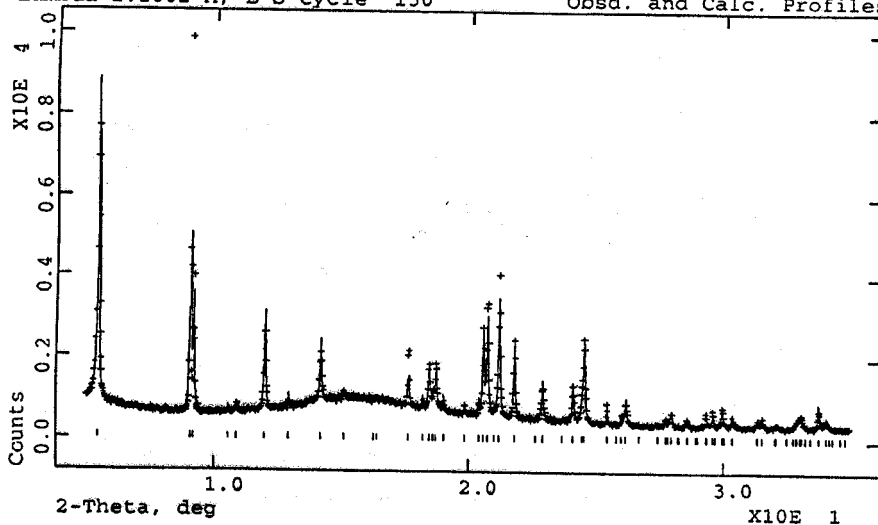
A Rietveld refinement on ETS-4 data was carried out using GSAS⁸ (also available at SNBL) starting from the superposition structure model of zorite³ in space group *Cmmm*. A reasonable good fit was obtained (see Figure) showing that the ETS-4 structure is very closely related to that of zorite. However half occupancies were refined for the positions of Si and Ti in the $4\text{SiO}_4/\text{TiO}_6$ groups inside the 12-ring channels. These suggest that, contrary to what happens in zorite, an ordered alternation of empty and filled 12-ring channels occurs in ETS-4. Moreover the presence of 'strong diffuse reflections' reported by Sandomirskii and Belov³ as a further evidence of the 'disorderly arrangement' in the zorite structure is not observed on diffraction pattern of the ETS-4 sample in this study.

Therefore a series of Rietveld refinements have been started based on structural models calculated for all the possible ordered varieties of zorite structure. This work as well as the direct methods analysis for *ab-initio* structural determination are still in progress.

ETS4 n.7 - SNBL 10.08.96

Lambda 1.1002 Å, L-S cycle 150

Obsd. and Calc. Profiles



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