



ESRF

Experiment title:  
CRYSTAL STRUCTURE OF ZEOLITE FERRIERITE  
IN AS-SYNTHESIZED, NH<sub>4</sub>- AND H-FORMS

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**Report:**

**INTRODUCTION**

Ferrierite is known to be a natural as well as a synthetic zeolite. The ferrierite framework contains two systems of mutually perpendicular one-dimensional channels of 10- and 8-membered rings. The crystal structure of a natural Mg-rich ferrierite was solved in the orthorhombic *Immm* space group<sup>1</sup>. Mg-rich ferrierites are characterized by the presence of a Mg(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> octahedron at the center of the so-called 'ferrierite-cage'<sup>2,3</sup>. A monoclinic symmetry, space group *P2<sub>1</sub>/n*, was reported for a natural Mg-poor, Na-, K-rich ferrierite<sup>4</sup>. The reduction of symmetry from *Immm* to *Pmnn* has been suggested in template-containing all-silica ferrierite<sup>5</sup>, and *Pmnn* structure refinements of synthetic all-silica ferrierites have been published using single crystal and Rietveld methods<sup>6\*</sup>.

The present paper is devoted to clarifying the structural modifications that ferrierite underwent during the NH<sub>4</sub>-exchange and calcination processes. Our particular interest is focussed on the following topics:

- 1- Determination of the space group of the synthetic low-silica, normally Mg-poor, ferrierite (*Immm*, *P2<sub>1</sub>/n*, *Pnmm*, *Pmnn* or others) in the as-synthesized, NH<sub>4</sub>-exchanged and rehydrated H-forms.
- 2- A detailed analysis of the distortions undergone by the framework of the as-synthesized ferrierite when it transforms into its NH<sub>4</sub>- and H-forms.
- 3- Location of: a) the extraframework cations (K, Na) and water molecules in the as-synthesized form; b) the NH<sub>4</sub><sup>+</sup> groups and water molecules in the NH<sub>4</sub>-form; c) the water molecules in the rehydrated H-form.

**EXPERIMENTAL SECTION**

Room temperature synchrotron X-ray powder diffraction data were collected on three samples of a low-silica ferrierite (Engelhard - ferrierite EZ<sup>TM</sup>-500) in the following forms: a) 'A-S-FER': the as-synthesized form (K<sub>2.7</sub>Na<sub>1.1</sub>Si<sub>32.2</sub>Al<sub>3.8</sub>·12H<sub>2</sub>O; Si/Al=8.5); b) 'NH<sub>4</sub>-FER': the NH<sub>4</sub>-form, as exchanged in a 1M solution of NH<sub>4</sub>NO<sub>3</sub> for 139 h at room temperature; c) 'R-H-FER': the rehydrated H-form, as obtained by calcinating

the  $\text{NH}_4$ -form at 550°C for 2 h, after it has been kept at room conditions for some months. Powder patterns were measured at the Swiss-Norwegian Beam Line (ESRF, Grenoble) on a triple axis diffractometer equipped with a Si(111) analyser crystal and operating in the Debye-Scherrer geometry. Rietveld structure refinements were performed by the GSAS package<sup>9</sup>.

## RESULTS AND DISCUSSION

The 'as-synthesized' form. The close inspection of the diffraction pattern of A-S-FER revealed the presence of weak reflections, which are forbidden in the *Immm* space group. The structure analysis was carried out in  $P2_1/n$ , starting from the positional parameters of the natural Mg-poor, Na-, K-rich ferrierite<sup>7</sup>. The final structure refinement ( $R_w = 6.7\%$ ;  $R_p = 5.1\%$ ;  $R_B = 5.8\%$ ;  $\text{red.}-\chi^2 = 5.3$ ) showed framework distortion leading to a significant displacement of tetrahedral atoms as compared to their expected positions in *Immm*. The shift of the O51 and O52 oxygens away from the inversion center, on which they are constrained in *Immm*, is equal to 0.46 Å along [001]. The O61 and O62 oxygens were also remarkably displaced along [100] of 0.25 Å, indicating a significant distortion of the 8-membered rings. This movement is consistent with the disappearing of the mirror plane perpendicular to [100], lowering the symmetry to  $P2_1/n$ . The largest electron density maximum is located near the center of the 8-membered rings (site I). The large occupancy fraction and bond distances from the first neighboring framework oxygens suggest that mostly potassium and sodium atoms are located in the I site. The I site is displaced away from the center of the 8-ring along [001] to allow a better coordination environment for (K,Na) atoms, and the ring itself is distorted along [100] to accommodate (K, Na). Both of these distortions imply lowering of symmetry to  $P2_1/n$ . The interaction of K and Na with the framework is mainly responsible for orthorhombic to monoclinic symmetry reduction in K- and Na-rich ferrierites. When the Mg-octahedron is present in the ferrierite cage, the I site must be vacant owing to the too short distance from one of the water molecules of the octahedron. In this way K and Na are excluded from the I site in Mg-rich ferrierite, and are therefore located within the 10-membered ring channels. In the absence of Mg, K and Na clearly show the greatest affinity for the I site.

The  $\text{NH}_4$ -exchanged form. As commonly recognized,  $\text{NH}_4$ -exchange causes a significant enlargement of the unit cell volume. Since the *I*-centering forbidden peaks were absent in the diffraction pattern of  $\text{NH}_4$ -FER, the *Immm* space group was adopted in this refinement ( $R_w = 6.6\%$ ;  $R_p = 5.2\%$ ;  $R_B = 7.3\%$ ;  $\text{red.}-\chi^2 = 4.0$ ). As previously reported, the *Immm* space group provides a satisfactory description of the average crystal structure of ferrierite when the static disorder of atoms is within the range of the ordinary thermal motion. The largest electron density maximum was located by the Fourier map in a position near the I site in A-S-FER, and refined at the center of the 8-ring. Taking into account the crystal chemical similarity between K and  $\text{NH}_4^+$  ions, we might suggest that a complete substitution of (K,Na) atoms by  $\text{NH}_4^+$  groups occurred, and that almost 80% of the I site is populated by  $\text{NH}_4^+$ . Due to the smaller ionic strength of  $\text{NH}_4^+$  compared to K, the decreased interaction between extraframework cations and framework oxygens, related to the removal of (K, Na) atoms, is also reflected in the restoring of the (pseudo-)*Immm* symmetry. A detailed analysis by Fourier methods, to locate possible protons around the I site in  $\text{NH}_4$ -FER, using both synchrotron X-ray and neutron data, is in progress, and will be discussed in a future paper.

Rehydrated H-form. The unit cell volume of R-H-FER is slightly contracted with respect to that of  $\text{NH}_4$ -FER, but in any case larger than that of A-S-FER. Similarly to what is observed in  $\text{NH}_4$ -FER, the diffraction pattern of R-H-FER shows no *I*-centering forbidden peaks. The crystal structure, refined in the *Immm* space group ( $R_w = 5.7\%$ ;  $R_p = 4.4\%$ ;  $R_B = 7.4\%$ ;  $\text{red.}-\chi^2 = 4.2$ ), is very similar to that of  $\text{NH}_4$ -FER. It appears that a minimal rearrangement of the extraframework content has occurred in such a way that the previous  $\text{NH}_4$  positions are replaced by water molecules with statistical occupancy.

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