

MS38-P2 Combining the powers of electron diffraction, electron microscopy, PXRD and NMR for structure determination of complex disordered zeolites

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Intergrowth and stacking disorders are common in inorganic materials in general and within zeolites in particular. Severe disorder makes structure determination a great challenge. Recent developments in electron crystallography facilitate the study of disordered materials greatly. In combination with powder x-ray diffraction and NMR these methods have proven to be successful in the structure determination of the new heavily disordered zeolite structure ITQ-39 [1].

Electron crystallography is highly complementary to x-ray diffraction with two big advantages. Firstly single crystal diffraction data can be obtained from crystals smaller than 50 nm by utilizing the Rotation Electron Diffraction (RED) method [2]. Single crystal data makes it much easier to analyze material and obtain information such as the unit cell, symmetry and also general knowledge about the nature of the disorder. A second great benefit of electron crystallography is the possibility to obtain high resolution transmission electron microscopy (HRTEM) images; images which reveal the local arrangement of atoms in the material without averaging and are of huge importance in the study of disordered materials.

The zeolite ITQ-39 exhibits a PXRD pattern with few and broad features, Fig 1, due to disorder and small crystal size, 30x30x500 nm. RED data indicated presence of stacking disorder, as diffusely scattered lines, and twinning. HRTEM images along two perpendicular directions revealed the local atomic arrangement and confirm the stacking disorder and twinning. Crystallographic structure factors were extracted from ordered regions of the images, regions as small as a few unit cells. The structure factors were merged into a 3D potential map from which the atomic structure could be determined. The material turned out to be a new zeolite family built from a random intergrowth of three different polytypes.

The material was synthesized in the presence of F⁻ ions which are trapped inside small cages of the structure. ¹⁹F NMR can provide a fingerprint for the type of cages present in the structure showed the presence of two different types of cages, the 4⁶ and the 4³5⁴ cages. The two cages can be assigned to the different polytypes and confirm their presence.

References

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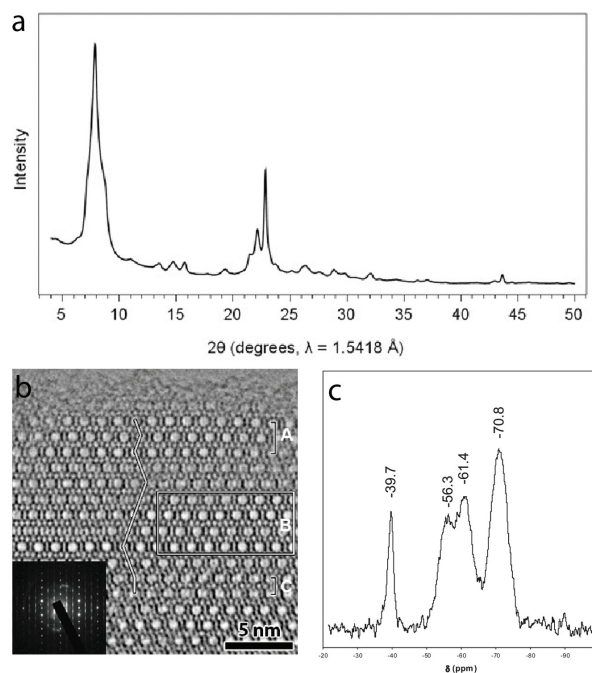


Figure 1. (a) PXRD pattern of the disordered zeolite ITQ-39 shows few and broad features. (b) A structure projection image reconstructed from HRTEM images reveals the local arrangement of atoms. (c) ¹⁹F NMR spectrum from ITQ-39 shows a fingerprint of 4⁶, 39.7ppm, and 4³5⁴, the other peaks.

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