MS047.O04

Disordered zeolite solved by combining electron diffraction, HRTEM and XRPD

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Zeolites are porous materials with important industrial applications. They are synthesized and used in polycrystalline form, and have complex, sometimes disordered structures, which makes their structure characterization difficult using conventional methods. IM-18 is a germanosilicate zeolite that was discovered more than 8 years ago, but its complex structure has remained elusive [1]. To determine its structure, we combined rotation electron diffraction (RED) [2] with high-resolution transmission electron microscopy (HRTEM) and powder X-ray diffraction (PXRD). The RED method combines discrete goniometer tilt (2.0-3.0°/step) with fine beam tilt (0.05-0.20°/step) to collect 3D ED data from a single nano-sized crystal. Although the 3D reciprocal lattice clearly showed diffuse streaks, indicating the presence of disorder, the average structure of IM-18 could be solved using direct methods. Characterization of the disorder using HRTEM proved difficult, because germanosilicates are sensitive to radiation damage. Therefore, we have developed a method for structure projection reconstruction from a through-focus series of HRTEM images acquired with a constant step of defocus changes, implemented in the program QFocus [3]. The structure projection reconstruction method is ideal for beam sensitive materials, because it allows fast data collection without the need of manually optimizing the defocus. The contrast of the reconstructed HRTEM image is greatly improved and the image can be directly interpreted in terms of structure projection. Several through-focus series of 12 HRTEM images with a defocus step of 85.3Å were taken along the b-axis of IM-18, and the structure projections were reconstructed using QFocus (Fig. 1C). By combining this information with the RED data, we were able to understand the structure and disorder of IM-18 and to refine its structure against the synchrotron XRPD data. The crystal structure of IM-18 is monoclinic (P2/m) with a = 10.509(5) Å, b = 14.943(5) Å, c = 17.774(9) Å, β = 107.29(6)° (Fig. 1A). The average structural model obtained from the RED data indicated the presence of disorder in the sample, because the double-4 rings (d4rs) are too close to each other and cannot exist simultaneously. IM-18 contains three-dimensional intersecting channels along a-, b- and c-axis defined by 8, 10, 8 vertex-sharing (Ge, Si)O4 tetrahedra, respectively. Rietveld refinement (Fig. 1B) helped to understand the average disorder in IM-18, indicating that there are two domains related by a shift of 1/2a. Further refinement revealed the location of the organic structure directing agent (OSDA) within the channel system.

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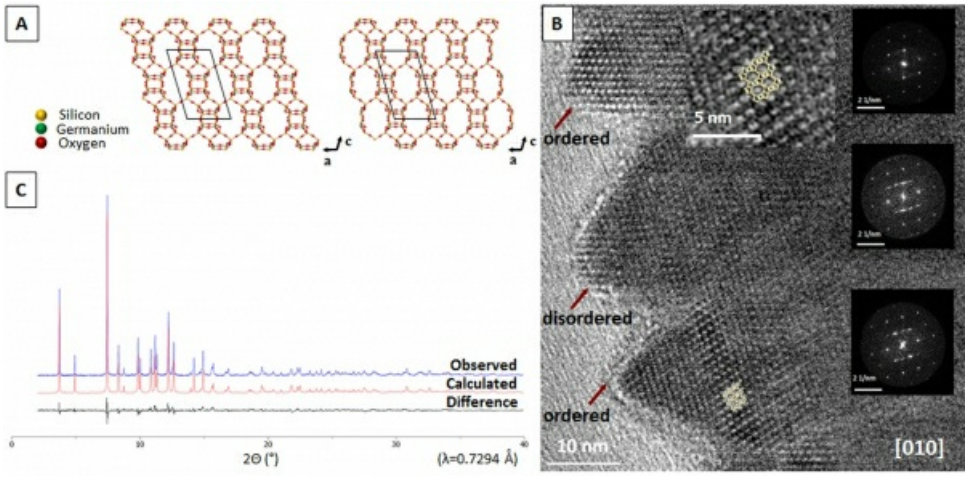

Keywords: zeolites, electron diffraction, structure determination