3D electron diffraction tomography studies of titanosilicate framework

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Microporous titanosilicates have been of interest not only due to the presence of the mixed octahedral-tetrahedral framework and elements other than Si and Al but also due to their perspective catalytic and physical properties. Many microporous compounds have a lot of defects due to the nature of their crystal structure. One of the representatives in the microporous titanosilicates family is ETS-10 with a framework that contains −Ti−O−Ti−O− chains and has three-dimensional 12-ring pore system with straight pores and pores that are bent due to the faulting [1].

In this work we investigated the structure of ETS-10 by the recently developed three-dimensional automated electron diffraction tomography (3D EDT) [2] (Fig 1). Sweeping reciprocal space is implemented by using the electron beam tilt in a given angular range with a small step. The beam tilt is combined with the crystal tilt in order to cover the full range of tilt angles available for the accessible transmission electron microscope (TEM) goniometer. The availability of a single tilt sample holder made it possible to collect 1530 individual selected area electron diffraction frames from the same nano-sized single crystal. The beam tilt step used in the data collection experiment was 0.15°. The total range of angles covered by the goniometer was from –62.7° to +68.9° (~132° in total).

Strong diffuse scattering was observed in the ED pattern frames due to extensive faults present in the material (Fig 1, right). The basic structural unit is a rod consisting of tetrahedral SiO_4 and octahedral TiO_6. From this unit the structure of ETS-10 can be described as a family of polymorphs (polymorph B in our case), many of which can be observed locally by HREM [1].

The crystal structure model of the ETS-10 B-polymorph (s.g. *C*2/*c*, a=b=21Å, c=14.51Å, β=111.12°) proposed in [1] was used as a starting structural model for the investigation of the nature of the diffuse streaks observed on the ED frames. From the reconstructed 3D reciprocal space we were able to conclude that the diffuse streaks appear only in the direction of the c* axis. The proposed model of random stacking along [1–10] was used to build a super-cell with 40 units along the [001] direction. This cell was further fed into the simulation and visualization program eMap [3] in order to obtain a kinematical diffraction pattern (Fig 2). We were able to get a good match between the experimental and the simulated pattern calculated using the proposed random stacking model.

The preliminary kinematical refinement of the crystal structure (not including the diffuse scattering) against the integrated intensities extracted from reconstructed 3D reciprocal space resulted in the R-factor ~35%.

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References

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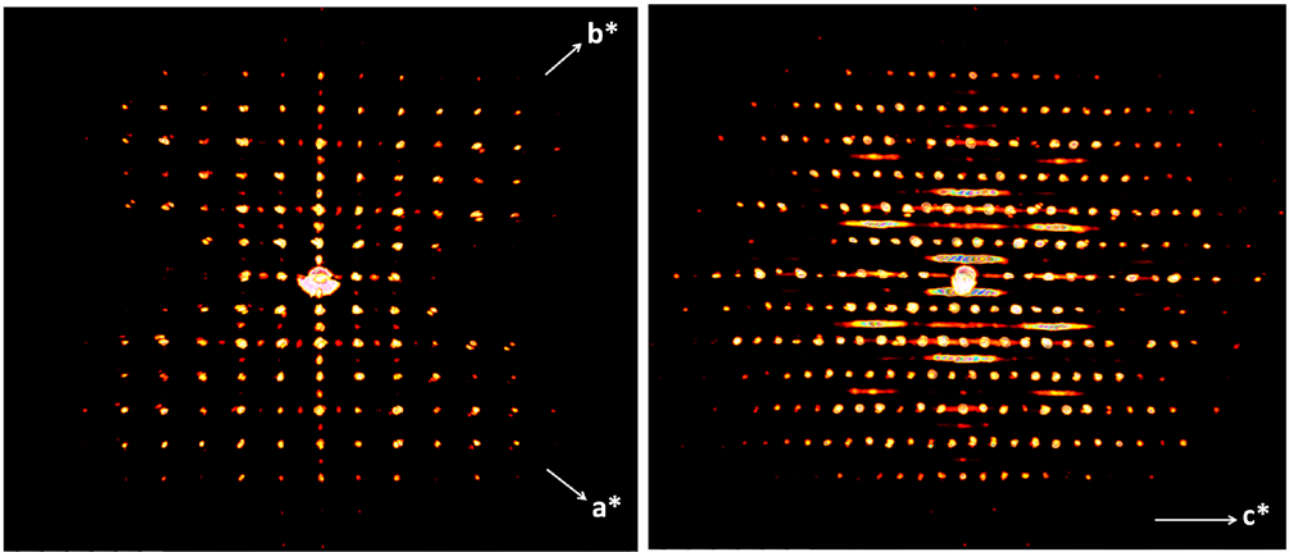

Figure 1. *3D reciprocal space reconstructed from 1530 individual ED frames (~132°). Left – view along the c* axis. Right – view along [1–10] direction. The diffuse scattering between main spots can be clearly observed as streaks along the c* axis only.*

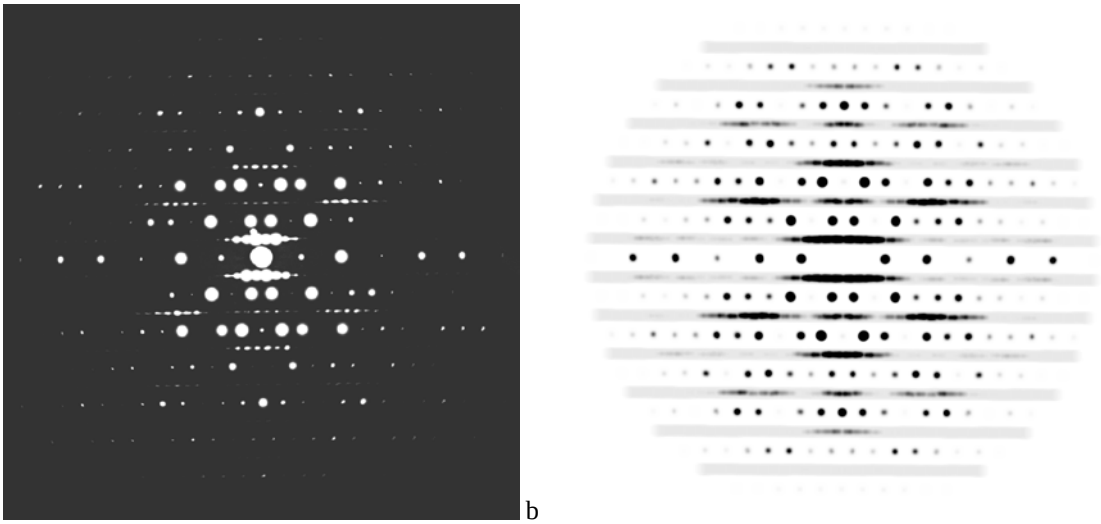

Figure 2. *A (110) slice of reconstructed 3D reciprocal space (left) and corresponding kinematical simulation of the twinned structure (right). See text for the details.*