MS004.O003

Determination of very beam-sensitive zeolite ITQ-57 by energy-filtered Timepix data

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In the last years, electron diffraction tomography opened new perspectives for the structure characterization of nanocrystalline materials. Electron diffraction can now be considered a routine option for ab initio structure determination and refinement in the case of materials that cannot be obtained as crystals large enough for single crystal X-ray diffraction and have structures too complex for being solved by powder X-ray methods alone. Still, the main factor limiting electron diffraction is the rapid amorphization of many materials under the electron beam, a common situation for organic, water-containing or porous materials. Here the necessity of strategies able to minimize the electron dose on the sample, either by speeding the acquisition time and/or by decreasing the illumination and the dose-rate.

These requests can be met combining STEM imaging for crystal search and centering, fast-EDT (FEDT) data acquisition while the sample is continuously tilting and the adoption of a Timepix-like single-electron detection device for recording the diffraction patterns [1]. In particular, combining the Timepix detector with an in-column energy-filter, it is possible to cut almost completely the inelastic scattering, and therefore to obtain background-free diffraction patterns. This allows a significant lowering of the dose-rate without a quality loss of the diffraction signal.

In the inorganic world, zeolites and other porous framework materials look very promising candidates for low-dose electron diffraction methods. In fact, beside their intrinsic beam sensitivity, many porous materials are not stable in wet atmosphere after removing the organic moieties from their channels, and cannot be easily transferred to the microscope for characterization. Therefore, for TEM-related investigations it is necessary to consider the non-calcined sample, with the building organic template, extremely beam sensitive and that can be only partially ordered, still inside the channels [3].

Last year, the beam-sensitive triclinic zeolite ITQ-58 was solved on the basis of FEDT data acquired in conventional TEM illumination mode [2]. More recently, we succeeded in solving ab initio a more complex and more beam sensitive zeolite, ITQ-57 (sg. Amm2; cell parameters: a ~ 13.1 Å, b ~ 14.8 Å, c ~ 53.3 Å). Data up to 0.7 Å resolution were acquired by a stepwise acquisition employing a 5 μm condenser aperture, even without the need of cooling the sample. Crystal searching and tracking were done in STEM mode and data were collected at the minimum illumination possible for our ZEISS Libra 120 kV TEM by a Timepix detector after cutting the inelastic signal by an in-column Ω-filter. Remarkably, previous attempts to record electron diffraction data in TEM illumination mode by stepwise and fast routines resulted in very incomplete and poor data sets, eventually not suitable for structure determination, due to the severe beam damage produced on the sample.

The structure of ITQ-57 is characterized by a 3D network of pores with diameter up to about 11 Å and, like ITQ-43 [3], by Q3 dangling Si sites where the organic template eventually attaches. The structure was subsequently validated and refined by the Rietveld method against laboratory powder X-ray diffraction data.

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Keywords: electron diffraction tomography, zeolite, beam-sensitive materials