Quantitative High-Resolution TEM/STEM and Diffraction

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Stucture determination with novel ultra-fast automated TEM 3D precession electron diffraction tomography technique

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TEM based 3D precession electron diffraction (PED) tomography technique [1] is a very useful technique for structure determination of nanocrystals that cannot be crystallized big enough to be studied with X-Ray diffraction. Using this technique, a series of ED patterns are collected in a TEM every 1° while the sample is tilted around the goniometer axis but a drawback of the technique is that is time consuming mainly due to the time needed for crystal position tracking after every tilt and CCD slow speed data collection. An automated procedure of 3D diffraction tomography is reported for some TEM platforms, where crystal tracking is performed in STEM mode and the diffraction is collected in nanobeam mode [1, 2]. Although the latter automatic procedure reduces data collection time compared to the conventional PED data collection techniques, acquisition time remains between 1-2 hours and this can be harmful especially for beam sensitive materials (zeolite, hybrid mesoporous crystals, organic crystals, etc).

Herein, an ultra-fast automated precession assisted 3D electron diffraction tomography method is presented, where PED data can be collected about 10-20 times faster compared to hitherto 3D diffraction tomography procedure. We observed that by tilting the TEM holder using 3D tomography, the sample is moving along a definite direction for a specific (quite large) tilt range and consequently, that such crystal movement could be tracked by shifting the beam (instead of tracking the crystal) along the same direction. During the simultaneous beam movement and crystal tilt the patter could be recorded by the CCD bottom mounted camera. The procedure is made possible by the ASTAR control unit for TEM [3,4], which allows to scan a rectangular area with a certain scan step (from 1 to several 100 nm) and collect a PED pattern at each point. As a proof of concept we performed an entire PED 3D tomography experiment on a $MgMoO_4$ crystal by recording a total of 99 patterns on a Zeiss Libra 120 using a 16 bit CCD camera 2k x 2k bottom mounted, using 1° precession angle. Sequential PED collection (with angular resolution 0.9°) was performed during the time required for TEM goniometer to cover the 92° tilt angle (tilt range from -54 to +38° performed in a continuous way) and lasted only 5 min 20 sec. To track crystal movement during TEM stage tilt, a linear area of 3.15 nm was scanned with ASTAR using 0.3 nm step size.

Collected PED data were processed with the ADT3D [2] and PETS [5] software to obtain unit cell parameters. Diffraction intensities measurement and hkl file extraction was carried out by ADT3D software. 3D reciprocal cell reconstruction for $MgMoO_4$ (fig.1) confirmed monoclinic unit cell with space group C2/m and cell parameters have been obtained with an error of less than 1% compared to the reference structure [6], (in parenthesis are reference structure parameters) a=10.211 Å (10.273), b=9.229 Å (9.288), c=7.080 Å (7.020), □=90.194° (90°), □=107.79° (106.950°), □=90.10° (90°). Structure solution was carried out using SIR2011 software using 714 independent reflections and allowed the complete structure to be solved (9 atoms into the asymmetric unit) with final R factor value of 31.96 %, which is a reasonable value for solved structures with ED data. Atomic positions are found very close to the X-Ray refined ideal positions (table 1). It is interesting to note that a similar conditions collection without using PED did not lead to any structure solution

This novel ultra-fast automatic 3D PED diffraction tomography approach can be considered as a breakthrough technique in electron crystallography as it is the first genuine full automated tomography method that could be performed for every commercial available TEM, provided that crystal shift during a specific tilt range is stable and reproducible. The technique help to hugely reduce 3d tomography ED data collection time and most importantly, may allow the application of TEM based 3D tomography to beam sensitive materials.

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		Reference Structure			Ultra-fast PEDT		
		x	y	z	x	y	z
Mo	Mo1	0.5000	0.2510	0.5000	0.5000	0.2545	0.5000
Mo	Mo2	0.7291	0.5000	0.0957	0.7289	0.5000	0.0915
Mg	Mg1	0.5000	0.1784	0.0000	0.5000	0.1838	0.0000
Mg	Mg2	0.7996	0.5000	0.6431	0.8050	0.5000	0.6534
O	O1	0.5415	0.1533	0.3040	0.5418	0.1668	0.3065
O	O2	0.3587	0.3561	0.3912	0.3481	0.3529	0.3783
O	O3	0.8587	0.5000	0.0391	0.8536	0.5000	0.0413
O	O4	0.6337	0.3448	0.0283	0.6339	0.3410	0.0256
O	O5	0.2983	0.0000	0.3551	0.3244	0.0000	0.3802

Table 1. Atomic position of the reference structure & the Ultra-Fast PEDT crystal structure determination

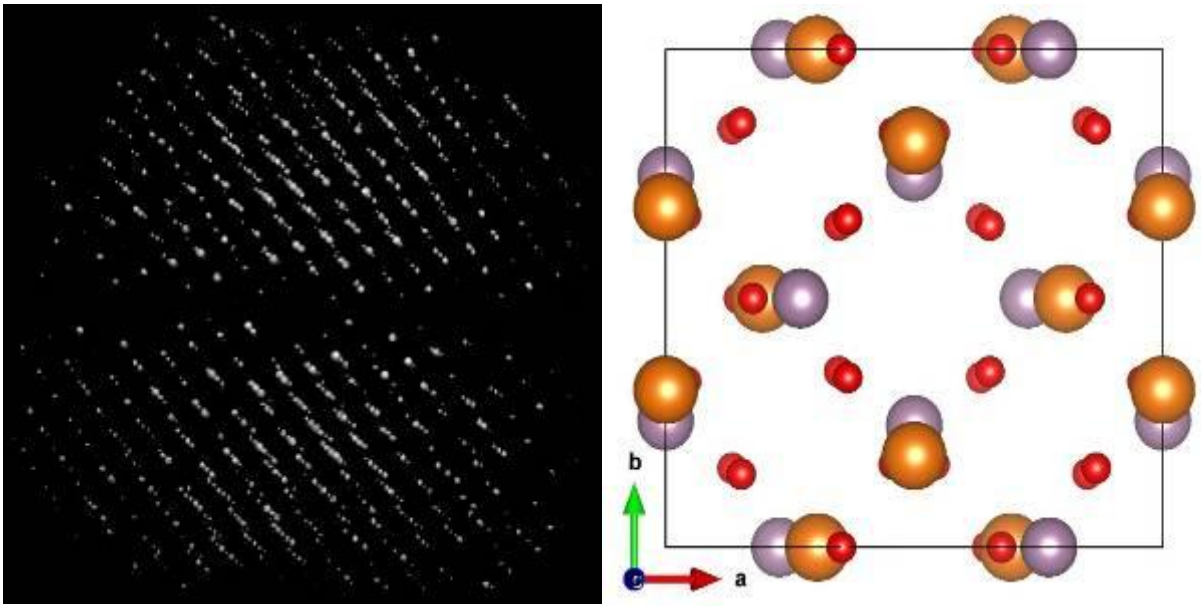

Figure 1. Reconstruction of 3D reciprocal space and structure model of $MgMoO_4$ using the ultra-fast automated 3d PED tomography data acquisition. Labels: Brown Mo , Grey Mg , Red O