MS41 The use of X-ray, electron and neutron scattering in nanoscience

Chairs: Christian Lehmann, Julian Stangl

MS41-O1 Complementarity of TEM to bulk diffraction techniques for structures at nanoscale

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When a structure cannot be satisfactorily solved/refined from X-ray or neutron diffraction, advanced transmission electron microscopy techniques (but also sometimes the conventional ones) can often help. Typical problems might arise from local order, weak reflections disappearing in background noise, atoms that scatter weakly in XRD, ... Using examples of problems we faced in the structure solution and refinement of different inorganic materials, the possibilities of several transmission electron microscopy techniques will be exposed.

First of all, high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) and annular bright field (ABF) STEM can be used to directly visualize the structure, much more easily understandably than was possible with conventional high resolution transmission electron microscopy. This can then be combined with high resolution energy dispersive X-ray analysis (EDX) and electron energy loss spectroscopy (EELS) with which we can do spectroscopy at atomic resolution. We will show some representative examples where these techniques were used: to characterize the cation order in $Sr_3Fe_2TeO_9$ (unexpectedly different from literature) , to solve intricate modulations and to map the different coordinations of the same element in crystallographic shear plane structures[1], to detect previously unnoticed atoms in "$K_2Nb_8O_{21}$"[2], to display small shifts of light atoms in $(Bi,Pb)FeO_3$[3], ...

Furthermore, the conventional technique of electron diffraction underwent an update into electron diffraction tomography[4], giving for each crystal a set of hkl with intensities reliable enough for structure solution and often even refinement. This can be used a.o. for characterizing nanocrystals, for the structure solution and refinement with elements that interact weakly with X-rays but more strongly with electrons, for samples where different phases cannot be separated (for example charged battery materials),... Here, we will show a case where all these difficulties occurred in combination and where the structure could only be successfully refined using electron diffraction tomography, i.e. charged and discharged lithium based battery materials.

References: [1]D. Batuk et al., Acta Cryst.B71(2015)127–143; [2]R. Paria Sena et al., Dalton Transactions 45 (2016)973-979; [3]W. Dachraoui, Chem. Mater. 24(2012)1378–1385; [4]U. Kolb et al, Ultramicroscopy 107(2007)507-513

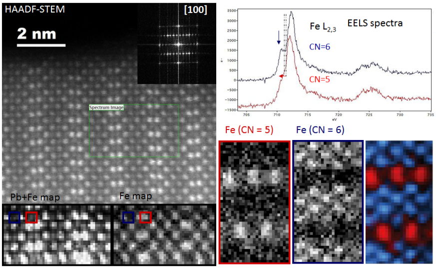

Figure 1. HAADF-STEM image of the $Pb_2Sr_2Bi_2Fe_6O_{16}$ structure with an Fe elemental map and maps of the Fe cations in octahedral (blue) and square pyramidal (red) coordination. [1]

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