

MS27-O2 Accurate unit cell determination from rotation electron diffraction dataWei Wan¹, Hong Chen¹, Jie Su¹, Sven Hövö¹

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3D electron diffraction tomography (EDT), for example automated diffraction tomography (ADT)[1] and rotation electron diffraction (RED) [2-3], have been very successful as a complimentary method to X-ray crystallography in studying complex structures of crystals of sub-micrometer sizes. However, due to lower data quality the EDT methods often need to be combined with powder X-ray diffraction (PXRD) for complete structure determination. For example, unit cell parameters and structure models are usually refined against PXRD data for better accuracy.

In this work we focus on improving the accuracy of unit cell determination from RED data. Depending on data quality, the errors in unit cell determination from RED data can reach 1-2% in lengths and 1-2 degrees in angles. This may lead to difficulties in the initial identification of crystal symmetry and subsequent structure solution. As RED uses difference vectors among the reflections from reciprocal space reconstruction for unit cell determination, the accuracy of unit cell determination is dependent on the accuracy of the reconstructed reflection positions. We developed a procedure where the unit cell parameters are refined against the inter-reflection distances in 2D electron diffraction frames. This makes use of the fact that after data processing all the indices of the reflections in the original 2D frames are known and the refinement can be done using the known inter-reflection indices. We show with a test data that after correcting the geometric distortions of the 2D frames [4], the inter-reflection distances can be measured accurately and the refined unit cell parameters reach an accuracy of ~0.1% in lengths and 0.1-0.2 degrees in angles.

[1] U. Kolb et al, *Ultramicroscopy* 107 (2007) 507[2] D.L. Zhang, et al, *Z. Kristallogr.* 225 (2010) 94[3] W. Wan et al, *J. Appl. Crystallogr.* 46 (2013) 1863[4] E. Mugnaioli et al, *Am. Mineral.* 94 (2009) 793**Keywords:** rotation electron diffraction, unit cell**MS27-O3** Study of partial occupancies and Jahn-Teller distortions in $(\text{Na}, \square)_5[\text{MnO}_7]_{13}$ by XRPD Rietveld and electron diffraction dynamical refinementsEnrico Mugnaioli^{1,2}, Mauro Gemmi², Marco Merlini^{3,4}, Michele Gregorkiewitz¹

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Manganese octahedral molecular sieves (OMS) are characterized by framework structures made of channels walled by MnO_6 octahedra and hosting different ionic species. A variable manganese oxidation state is found together with a wide structural variety of framework connectivity and pore sizes [1]. OMS are extensively investigated because their mixed electronic/ionic conductive properties, which in turn depend on structurally related features, like Mn^{4+} - Mn^{3+} ordering and coordination number of extra-framework ions. Nonetheless, a systematic structure characterization of OMS by X-ray methods is hampered by difficulty in growing single crystals and achieving pure synthetic products.

$(\text{Na}, \square)_5[\text{MnO}_7]_{13}$ is a well-known electrode material, whose structure has long been associated with a romanèchite-like framework. Recently, the structure of $(\text{Na}, \square)_5[\text{MnO}_7]_{13}$ was re-determined *ab initio* by precession-assisted Electron Diffraction Tomography (EDT) in space group $C2/m$, resulting in a completely novel framework hosting 3 independent Na sites inside the channels [2].

The structure was subsequently refined vs laboratory and synchrotron XRPD data by Rietveld method, and vs EDT data by both kinematical and dynamical methods [3]. Laboratory XRPD data and EDT kinematical refinement confirmed the correctness of the *ab initio* model, but MnO_6 octahedra proved rather distorted and no information about possible crystallographically-related distribution of Mn^{3+} in the framework could be obtained.

Conversely, structures refined on the basis of synchrotron XRPD data ($R_{\text{wp}}=0.051$, $R_{\text{p}}=0.037$, $R_{\text{F2}}=0.036$) and EDT dynamical refinement ($R_{\text{Fobs}}=0.07$) converged on very close models. The average and maximum discrepancies between the two coordinate sets were 8 and 21 pm respectively (3 and 5 pm respectively for Mn atoms). Na coordination shells were well-defined and occupancies refined to values close to expected stoichiometry. One MnO_5 square pyramid and two MnO_6 octahedra were characterized by longer average interatomic distances and Jahn-Teller distortion, consistent with manganese in oxidation state (3+). Distribution and multiplicity of Mn^{3+} and Na sites in the structure satisfactorily explain the electro-chemical behavior of $(\text{Na}, \square)_5[\text{MnO}_7]_{13}$, which could not be understood assuming the former romanèchite model.

[1] Pasero, M. (2005). *Rev. Mineral. Geochem.* 57, 291-305.

[2] Mugnaioli, E. *et al.* (2016). *J. Power Sources*, under revision.

[3] Palatinus, L. *et al.* (2013). *Acta Cryst. A* **69**, 171–188.

Keywords: electron diffraction tomography (EDT), dynamical refinement, synchrotron Rietveld refinement, octahedral molecular sieves (OMS), electrode materials

MS27-O4 Localization of hydrogen atoms in organic molecules using dynamical refinement of electron diffraction data

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Although, localization of hydrogen atoms in data from electron diffraction has been reported in special cases [1,2] reliable *ab initio* determination of hydrogen positions from single nano-crystals has not been achieved to the best of our knowledge. Our work focuses on pharmaceuticals and pharmaceutical co-crystals. The stability of these compounds under electron beam irradiation is low and data collection requires low-dose technique at low-temperature. Precession assisted electron diffraction tomography on single nano-crystals was used for data acquisition. Data were processed using programs PETS, Jana2006 and Dyngo. In favourable cases like in the case of paracetamol form I (S. G. $P2_1/n$), it was possible to localize a few of the hydrogen atoms in difference Fourier maps after kinematical refinement of the structure ($R(\text{obs}) = 20\%$). Dynamical approach provided an improved difference Fourier map, which revealed the complete set of hydrogen atoms (Figure 1). Dynamical refinement of the structure without the hydrogen atoms resulted in the $R(\text{obs})$ factor of 12%. An addition of the hydrogen atoms into the model led to an additional improvement of the $R(\text{obs})$ slightly below 10%, demonstrating the sensitivity of the result to the presence of the hydrogen atoms in the model.

[1] Electron diffraction techniques, J. M. Cowley, Volume 1, Chapter 6 and references therein, Oxford University Press 1992.

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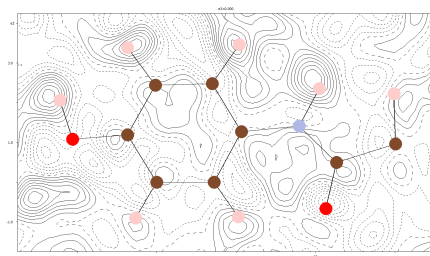


Figure 1. Difference Fourier map of the best plane through the paracetamol molecule overlaid by the structure obtained after refinement of the model with added hydrogen atoms.

Keywords: hydrogen atoms localization, single crystal electron diffraction, dynamical refinement