

**MS27-O2** Accurate unit cell determination from rotation electron diffraction dataWei Wan<sup>1</sup>, Hong Chen<sup>1</sup>, Jie Su<sup>1</sup>, Sven Hövö<sup>1</sup>

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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.

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- [2] D.L. Zhang, et al, Z. Kristallogr. 225 (2010) 94
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**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 refinements

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Manganese octahedral molecular sieves (OMS) are characterized by framework structures made of channels walled by  $\text{MnO}_6$  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  $\text{Mn}^{4+}$ - $\text{Mn}^{3+}$  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  $\text{MnO}_6$  octahedra proved rather distorted and no information about possible crystallographically-related distribution of  $\text{Mn}^{3+}$  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  $\text{MnO}_5$  square pyramid and two  $\text{MnO}_6$  octahedra were characterized by longer average interatomic distances and Jahn-Teller distortion, consistent with manganese in oxidation state (3+). Distribution and multiplicity of  $\text{Mn}^{3+}$  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.

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