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MS26 O3

Precession electron diffraction of Mn_2O_3 and $PbMnO_{2.75}$: solving structures where X-rays fail Holger Klein, *Institut Néel, MCMF, Grenoble, France*.

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X-ray diffraction has been used for nearly a century to solve crystal structures and the methods that have been developed make it the prominent method of structure resolution today. Structures have been solved from single crystals of a few tens of μm in diameter or even less using synchrotron radiation techniques. Powders, even if they contain more than one phase, have also been used for X-ray diffraction structure determination. However, with the trend in fundamental research and applications towards materials on the nanometre scale, X-ray diffraction reaches its limits for structure resolution more and more often. Single crystals of less than $1 \mu m^3$ are not suitable for X-ray diffraction experiments and powders always present the difficulty of peak overlap that in the case of complex phases often prevents the determination of the cell parameters, without even speaking of structure determination. In these cases electron crystallography can be a powerful tool for the determination of the atomic structures of crystals even though it remains a delicate and time consuming method. Its advantages are the fact that an individual nanometre-sized particle can be used as a single crystal for electron diffraction and in the possibility to obtain real space images of atomic resolution.

In this contribution we present two of these "real" cases. The first sample is a nano-sized powder of MnO_2 , which is interesting for applications in batteries, but which contained a few percent of an unexpected phase. Powder X-ray diffraction only showed a few weak additional peaks in the β - MnO_2 spectrum, which were insufficient for a phase determination. By electron diffraction we identified the minority phase to be pseudo-cubic α - Mn_2O_3 . The use of the recently developed precession electron diffraction technique yielded diffracted intensities close to the intensities expected in kinematical theory. The structure was then solved by applying the direct methods computer program SIR97. It should be noted that the use of standard selected area electron diffraction (SAED) data did not permit to solve the structure.

The second sample is a pure powder of $PbMnO_{2.75}$. This complex structure suffers from severe peak overlap in the X-ray powder diffraction pattern and the cell parameters could not be determined by this technique. SAED yielded the cell parameters and the space group of this phase and the study of a high resolution electron micrograph (HREM) allowed determining the positions of the anions in the structure [1]. The resolution of the micrograph is not sufficient to obtain the oxygen positions. However, the Fourier Transform of the HREM yields the phases of the structure factors which can then be combined with precession electron diffraction data in order to determine the oxygen positions. In this contribution we report on the results obtained.

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MS26 O4

Recent achievements in automated electron diffractometry Ute Kolb^a, Tatiana Gorelik^a, Max Otten^b, Dominique Hubert^b, Christian Kübel^c, ^a*Department of Physics, University of Mainz*. ^b*FEI Eindhoven, The Netherlands*. ^c*Fraunhofer Institute, Bremen, Germany*. E-mail: kolb@uni-mainz.de

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The ultimate aim of electron diffraction data collection for structure analysis is to sample the reciprocal space as accurately as possible to obtain a high quality data set for crystal structure determination. Besides a more precise lattice parameter determination, fine sampling is expected to deliver superior data on reflection intensities which is crucial for subsequent structure analysis. Traditionally, 3D diffraction data are collected by manually tilting a crystal around a selected crystallographic axis and recording a set of diffraction patterns (a tilt series) at various crystallographic zones. In a second step, diffraction data from these zones are combined into a 3D data set and analyzed to yield the desired structure information. An experimental software module¹, based on recent advances in tomography acquisition, has been developed for the Tecnai microscope for an automated diffraction pattern collection while tilting around the goniometer axis comparable to a ω scan in traditional single crystal X-ray diffraction data collection. The module combines STEM imaging with diffraction pattern acquisition in nanodiffraction mode. It allows automated recording of diffraction tilt series from nanoparticles with a size down to 5 nm. Data acquisition can be performed by a tilt around an arbitrary axis without any additional arrangement of the crystal and delivers a part of the reciprocal space where low-index crystallographic zones are found only accidentally. Through a combination of several tilts the reciprocal space can be sampled much better. Acquired electron diffraction tilt series are first subject to pre-processing including background subtraction, centring of diffraction patterns in each frame and rough orientation of the tilt axis. The pre-processed data can then be fully integrated into a huge reciprocal volume. Visual 3D inspection of this volume allows both to judge the general correctness of the data (single crystal data (?), appropriate position of the tilt axis (?), etc.) and to examine particular properties of the crystalline structure (superstructure, partial disorder, crystal twinning). Subsequently, the pre-processed data is analysed, as traditionally done in X-ray crystallography, via peak search in each frame, unit cell determination and orientation matrix construction. All routines however have to be specifically adopted for electron diffraction data. The automated electron diffraction module accelerates the data collection significantly which allows the investigation of multiphase systems in a reasonable time. Here we report on the basic principles of the diffraction module functionality, as well as we show first results on data processing.

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