## MS26 O1

**Precise Estimation of Structure Parameters from Electron Microscopy Images** Sandra Van Aert, Sara Bals, Gustaaf Van Tendeloo, Dirk Van Dyck *Department of Physics, University of Antwerp, Antwerp, Belgium.*
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**Keywords: electron microscopy, precision, quantification**

Electron microscopy allows to precisely determine unknown structure parameters. For example, the precision with which atom positions can be determined from electron microscopy images is comparable to the precision obtained from X-ray powder diffraction data. Furthermore, as a result of the strong interaction of electrons with the material under study, it is possible to obtain this information on a more local scale. However, in order to precisely determine unknown structure parameters, a quantitative, model-based method is required. The aim of this contribution is to introduce such a method and to demonstrate its practical applicability by means of recent experimental examples.

The key to precise structure determination is the availability of an expectation model, which is a, usually physics based, model describing the expectations of the image pixel values. In fact, the expectation model includes all the ingredients needed to perform a computer simulation of the images and it is parametric in the quantities of interest, such as the atom positions. Next, the unknown parameters of the model are estimated using statistical parameter estimation theory. This is done by optimizing a criterion of goodness of fit, such as the likelihood function or the least squares sum. This criterion quantifies the similarity between the observations and the expectation model. The parameters for which this criterion is optimal, represent the estimated parameters. A comprehensive report of this model-based method can be found in [1-2].

In one of the experimental examples which will be shown, the atom column positions of a new ceramic compound, $Bi_4Mn_{1/3}W_{2/3}O_8Cl$, have been determined with a precision in the picometer range [3]. Therefore, exit wave reconstruction combined with statistical parameter estimation has been used. The phase of the reconstructed exit wave reveals the light oxygen atoms in the presence of heavier atoms. Although the phase of the exit wave is often considered as the final result, it has been used as a starting point for quantitative refinement of the atom column positions. Therefore, a model has been proposed to describe the expectations of the pixel values in the reconstructed phase. The unknown parameters of this model, including the atom column positions, have been estimated in the least squares sense. Next, mean interatomic distances and their corresponding standard deviations have been calculated from the estimated atom column positions. The standard deviation, being a measure of the precision, ranges from 3 to 10 pm. Furthermore, a good agreement has been found when comparing these results with X-ray powder diffraction data. It is also found that projected distances beyond the information limit of the microscope (110 pm) can be determined with picometer range precision.

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## MS26 O2

**Symmetry study of $PbZr_{1-x}Ti_xO_3$ by Convergent-Beam Electron Diffraction** Roland Schierholz[a], Hartmut Fuess[a], Yoichiro Ogata[b] Kenji Tsuda[b], Masami Terauchi[b]
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**Keywords: CBED, crystallographic symmetry, ferroelectric oxides**

$PbZr_{1-x}Ti_xO_{3-}$ ceramics exhibit the highest values in piezoelectric constants close to the morphotropic phase boundary (MPB). At this boundary the crystal structure changes with composition and the material contains minute domain structures. These were reported to affect X-ray diffraction profiles the same way as a lower crystallographic symmetry [1].

To analyse the crystal symmetry of $PbZr_{1-x}Ti_xO_3$ over the MPB convergent-beam electron diffraction (CBED) was used. CBED enables us to determine local symmetries of a few nm-size specimen area. TEM-samples with compositions x = 0.40, 0.45, 0.46, and 0.48 were prepared by using ion-milling instrument (ion-slicer). CBED experiments were mainly conducted by using a transmission electron microscope JEM 2010 equipped with $LaB_6$.

To judgement on symmetry is based on projected Whole pattern (proj. WP) symmetry whole pattern (WP) symmetry including higher order reflections, as well as the symmetry of Dark field Patterns (DP's). The results for the two morphotropic compositions x = 0.45 and 0.46 show evidence for a monoclinic structure first proposed by Noheda *et al.* [2] based on fitting to X-ray powder diffraction profile.

For the x = 0.46 composition also heating experiments were performed and at ~300 °C tetragonal symmetry was observed. This result is again consistent with X-ray powder diffraction experiments by Noheda *et al.* [3].

For the compositions on the tetragonal x = 0.48 and on the rhombohedral side x = 0.40 of the MPB symmetries of CBED-patterns were not always clear as expected for the above named crystallographic symmetries of single crystalline materials of non-solid-solution systems. Since a breakdown of symmetry in CBED-patterns can be caused by several other influences, an interpretation of the results is not straightforward. Ideas for these influences and how to recognize some of them will be discussed.

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## MS26 O3

**Precession electron diffraction of $Mn_2O_3$ and $PbMnO_{2.75}$: solving structures where X-rays fail**

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**Keywords: electron crystallography, structure resolution, oxides**

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**

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**Keywords: electron crystallography, automated data collection, data processing**

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 module[1], 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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