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Complete 3D electron diffraction data collection - new methods and applications. Xiaodong Zou, Peter Oleynikov, Daliang Zhang, Tom Willhammar and Sven Hovmöller. *Inorganic and Structural Chemistry, Department of Materials and Environmental Chemistry, and Berzelii Center EXSELENT on Porous Materials, Stockholm University, Sweden.*
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Electron crystallography is a unique technique for structure analysis of crystals too small to be studied by single-crystal X-ray diffraction, even using a synchrotron radiation. Many different structures including the most complicated zeolites and quasicrystal approximants have been solved by electron diffraction (ED) and high-resolution transmission electron microscopy (HRTEM) combined with crystallographic image processing.[1] Even though, electron crystallography is not widely used for structure analysis compared to X-ray diffraction. The main reasons for this are 1) dynamical scattering; 2) incomplete data and 3) the techniques are not feasible and highly skilful operators are needed. The later often requires a long and hard training period. We have developed several new methods to tackle those problems.

Dynamical scattering may be reduced when the incident electron beam is tilted off the zone axes. This is achieved in precession electron diffraction (PED). We have developed a new software-based method – the digital sampling method to automatically collect a series of ED frames while the electron beam is precessed.[2] Several different post-processing strategies are developed for extracting the ED data and combining them to a PED pattern. The intensity data obtained by the digital sampling method were used for structure refinement of $K_2O \cdot 7Nb_2O_5$. The data quality is shown to be comparable to, and in some cases even better than that obtained using a hardware-based electron precession device.

We have combined digital electron beam rotations with goniometer tilts for collecting complete 3D electron diffraction data.[3] A 3D electron diffraction dataset with an tilt range of $\pm 70^\circ$ can be collected automatically from a nano-sized crystal on a JEOL JEM2100 TEM. More than one thousand electron diffraction patterns can be collected within 1-2 hours, with a step of $0.05^\circ - 0.1^\circ$ for each ED frame. There is no need for pre-alignment of the crystal. The ED patterns are combined into a 3D reciprocal lattice, from which the unit cell parameters and space group can be determined. ED intensities of all reflections can be extracted and used for structure solution and refinement. Diffuse scattering and diffraction streaks caused by crystal defects can be quantified and used for studying the defect structures in the crystals.

The power of the new methods for structure analysis is demonstrated on several inorganic structures and zeolites. The automation procedure for collection of complete 3D ED data from nano-sized crystals opens new possibilities and applications of electron diffraction for structure analysis.

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DFT Versus Accurate Experimental Measurements of Charge Density in Aluminium. Philip N.H. Nakashima^a, Andrew E. Smith^b, Barrington C. Muddle^a
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The term "density" in density functional theory (DFT), refers to the ground state charge density, which is the basis of this and other *ab initio* models of predictive chemistry. Therefore, the most effective test of all such models is a comparison between the bonding charge density that they predict for a particular material and a corresponding set of accurate experimental measurements.

Quantitative convergent beam electron diffraction (QCBED) is a well-matured technique for the absolute (scale and extinction free) measurement of Fourier coefficients of crystal potential (structure factors) in highly perfect crystals with small units cells [1]. Crystal potential structure factors are directly related to those of the electron density via the Mott formula and it is in the low orders that the conversion process further enhances the intrinsic precision and accuracy of QCBED. The low order structure factors are also those that are most sensitive to chemical bonding and are therefore the ones that should be compared with *ab initio* calculations, such as those based on DFT.

The present work summarises the most recent advances in QCBED, which have produced new modes of analysis that further improve the precision of structure factor measurements [2–4]. Application to pure aluminium in conjunction with a detailed DFT study has allowed a rigorous comparison of the bonding charge density measured by QCBED and that predicted by a variety of DFT calculations, in a material that is, theoretically, ideally suited to DFT.

The general view, that most of the bonding charge density resides in the octahedral interstices of aluminium [5–7], is called into question. The present results show that the main concentration occurs in the tetrahedral interstices instead. The latter configuration presents a number of strong correlations between the nature of bonding in pure aluminium and the nature of strengthening precipitates that form in aluminium alloys. This is an example of how detailed knowledge of a precursor charge density distribution can, at least in part, help explain the route of phase transformations that occur in the environment of a particular electronic structure.

Furthermore, the ability to chose the variant of *ab initio* modeling that best matches an accurate experimental determination of the ground state charge density in a material, will lead to a more educated reliance on solid state theory for the prediction of materials properties. This is a particularly important step for atomistic modeling of phase transformations in aluminium alloys and is one of the main reasons for the present study of pure aluminium.

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Keywords: quantitative convergent beam electron diffraction, DFT, charge density studies

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Structure solution in multiphase Sr-Bi-Ni-O powder by electron crystallography. Holger Klein^a, Pierre Strobel^a, Jérémy David^a, Amélie Rageau^a, Mauro Gemmi^b, Vladimir V. Pankov^c, Masha Golikova-Novitskaya^c, Leonid V. Makhnach^c. ^a*Institut Néel, Grenoble, France.* ^b*Dipartimento di Scienze della Terra 'Ardito Desio', Sezione di Mineralogia, Milano, Italy.* ^c*Inst. of General and Inorganic Chemistry, National Academy of Sciences of Belarus, Minsk, Belarus.*
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In multicomponent oxides of the transitional and rare-earth elements with perovskite structure (ABO₃, A = rare-earth, B = transition metal) it is possible to improve the physicochemical and electrochemical properties with cation substitution in sites A and B. In this aim perovskite-like oxides of Sr-Bi-Me-O systems (with Me = Cu [1-3], Co [4], Fe, Cr [5], Mn [6]) have been extensively studied. In this work we investigate the Sr-Bi-Ni-O system where no structures have been published in spite of the fact that it should be possible to obtain multicomponent oxides which exhibit superconducting properties or are suitable for oxide fuel cell and membrane production. The samples with nominal composition Sr₃Bi_{2-x}Ni_xO_{6-δ} were prepared from nitride precursors and calcined in air or oxygen current at 900 °C during 10 – 15 hours, followed by 20–30 hours at 1000 – 1200 °C. Transmission electron microscopy showed the existence of at least 3 different phases: a tetragonal phase ($a = 5.36 \text{ \AA}$, $c = 17.5 \text{ \AA}$), a closely related orthorhombic phase ($a_o \approx a_t / \sqrt{2}$, $b_o \approx a_t * \sqrt{2}$, $c_o \approx c_t$) and a minority cubic phase ($a = 33.6 \text{ \AA}$). EDX yielded the cation ratio to be 22.0% Ni, 64.2% Sr and 13.8% Bi for the tetragonal phase, the oxygen being too light to be analyzed. In the case of such a mixture of phases with related cell parameters X-ray powder diffraction is useless for structure determination. We therefore conducted an electron crystallography study on the tetragonal phase. Due to the close relationship with the orthorhombic phase only few zone axes permit to distinguish between these two phases. Therefore, we only considered data from a single particle clearly identified as the tetragonal phase in this study. A total of 13 different zone axes were each recorded in selected area electron diffraction mode and with different precession angles up to 4.1°. From the observed extinctions the space group was determined to be *I4/mmm* or *I4mm*. For the structure solution we extracted the intensities from the 8 main zone axes yielding a total of 109 independent reflections with a resolution of 0.8 Å. The data were corrected by a geometrical Lorentz type factor and the structure was solved ($R = 29\%$) using the SIR2008 program [7]. The solution contained all atoms except for one oxygen position. The structure can be described as formed by layers of edge sharing oxygen octahedra. The layers are connected via octahedron corners. In this contribution we compare the obtained structure to oxides containing other transition metal ions and discuss the subject of the missing oxygen position.

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Structure Analysis of Titanate Nanorods by Electron Diffraction. Iryna Andrusenko^a, Enrico Mugnaioli^a, Tatiana Gorelik^a, Ute Kolb^a, Dominik Koll^b, Martin Panthöfer^b, Wolfgang Tremel^b. ^a*Institute of Physical Chemistry, Johannes Gutenberg-University, Mainz, Germany.* ^b*Institute of Inorganic and Analytical Chemistry, Johannes Gutenberg-University, Mainz, Germany.*
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Structural information is essential for understanding physical and chemical properties of materials. In order to gain structural information from nano crystalline materials diffraction data from single nano grains should be collected. In these cases nano electron diffraction is the technique of choice, as it can probe single crystals as small as 20 nm. Nevertheless structure solution by electron diffraction is hampered by strong dynamical effects and limited number of sampled reflections. In order to reduce these drawbacks, routines for a quasi-continuous sampling of reciprocal space were developed by Kolb at al. (Automated Diffraction Tomography – ADT) [1, 2]. Since the first report on the “Formation of Titanium Oxide based Nanotubes” [3] this type of nano materials has been discussed intensively for its use in photocatalysis or as semiconductor electrode in dye sensitized solar cells. Preliminary investigations showed that there are different crystallographic phases formed in nano sized titania systems depending on the synthetic route. Structures of all these phases are important for understanding the mechanism of nano architectural formation and physical properties of the product. Here we present the structure analysis of the primary product in the synthesis of titania nano rods from titania upon hydrothermal treatment in concentrated caustic soda solution. The structure analysis was performed by a combination of ADT and precession electron technique [4]. Quasi-kinematical 3D electron diffraction data sets from single nano crystals were collected with a FEI TECNAI F30 transmission electron microscope. All analyzed crystals exhibited diffuse scattering. Nevertheless, an almost ordered crystal was selected for diffraction data collection. Lattice parameters were determined automatically by devoted routines. The structure was solved using direct methods implemented in SIR2008 and refined by ShelXL. The disorder was visualized and described by the 3D reconstructed reciprocal space.

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