

FA3-MS03-O3

Structure Determination of Complex Oxides. Joke Hadermann^a, Artem M. Abakumov^a, Hans D'Hondt^a. ^a*EMAT, University of Antwerp, Belgium.*
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The *ab initio* structure determination using precession electron diffraction will be discussed for different examples of complex oxides. The focus of the study is on the possibility to determine the oxygen positions in compounds containing heavy scattering elements. The effect of recording techniques, presence of heavy scatterers, cell volume, symmetry, and other aspects will be elaborated upon. The possibility to localize the oxygen atoms will be demonstrated using a relatively simple rutile type SnO₂ structure. The solution obtained with the precession electron diffraction data is in excellent correspondence with the structure refined from X-ray diffraction data. The application of the precession electron diffraction technique to more challenging structures will be shown using the examples of the Sr₃AlMn₂O_x phase (high unit cell volume, low symmetry) and the PbMnO_{2.3} phase (large unit cell volume, presence of very heavy scatterer such as Pb). For such compounds precession electron diffraction is a promising tool for obtaining structural information because conventional structure solution using powder diffraction data is hampered by the multiphase nature of the samples and the weakness of the superlattice reflections originating from the ordering of oxygen atoms and vacancies.

Keywords: precession; TEM; oxide

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Ab Initio Solution of LiTi_{1.5}Ni_{0.5}O₄ by Precession Electron Diffraction. Holger Klein^a, Mauro Gemmi^{a,b}, Amélie Rageau^a. ^a*Institut Néel, CNRS and Univ. J. Fourier, Grenoble, France.* ^b*Dipartimento di Scienze della Terra 'Ardito Desio', Sezione di Mineralogia, Milano, Italy.*
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Oxides are a vast class of materials presenting various properties used in different technological applications. You can find these materials in batteries, fuel cells, high Tc superconductors, multiferroics, etc. Many of the new phases in this field are synthesized at high temperature (HT) and under high pressure (HP). Single crystals suitable for X-ray diffraction are therefore rarely available and powder X-ray diffraction suffers from severe peak overlap. Even in the rare cases where the powders contain only one phase this hinders cell parameter determination and inhibits structure solution. Electron crystallography is then a powerful alternative for solving these structures.

The sample with nominal composition LiTi_{1.5}Ni_{0.5}O₄ was synthesized by solid state reaction for use in Li-batteries. The majority phase in this powder containing 3 phases was determined by electron diffraction to be of trigonal symmetry with space group *P3c1* or *P-3c1* and cell parameters $a = 0.505$ nm, $c = 3.25$ nm (hexagonal setting). PED data

were extracted from 10 different zone axes yielding 105 independent intensities. The structure solution obtained in the centrosymmetric space group *P-3c1* is composed of layers of oxygen octahedra formed by 4 independent oxygen positions. There are 6 independent positions for Ti and Ni occupying the centers of some of the octahedra. Discrimination between Ti and Ni proved to be difficult from these results. Two independent positions were found for the Li ions equally occupying oxygen octahedra. The solution is robust against changes in the process parameters always yielding the same positions including those for Li. Since crystal chemistry suggested either sites with a Ti/Ni disorder or a non centrosymmetric structure we also attempted a structure solution in the non centrosymmetric space group *P3c1*. Here the solution contained 12 independent Ni/Ti positions, 7 independent O positions and 4 independent Li positions. Comparing these positions to those obtained in the centrosymmetric case shows that they are identical even for the light Li ions.

A high resolution synchrotron radiation diffraction experiment was carried out on the powder on beamline ID31 at the ESRF in Grenoble, France. While an *ab initio* solution of the structure could not be obtained from the synchrotron data, we have used these data to refine the model obtained from PED.

Keywords: crystallographic structure; TEM; oxide

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Automated Diffraction Tomography - A New Tool to Access Structures From Nano Crystals. Ute Kolb^a, Enrico Mugnaioli^a, Tatiana Gorelik^a. ^a*Institute for Physical Chemistry, Johannes Gutenberg-University Mainz, Germany.*
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Automated diffraction tomography (ADT) [1, 2] complies a powerful and quick tool to determine cell parameters and possible space groups from fully unknown nano particles and furthermore to collect reliable electron diffraction intensities suitable for direct crystal structure analysis.

Collection of diffraction patterns is performed in nano electron diffraction (NED) using a 10 μm C2 aperture and crystal imaging for crystal tracking in μ-probe STEM mode. In contrary to traditional methods by using ADT there is no need to orient the crystal in any way. Data processing and analysis has been automated in self programmed, Matlab based routines in order to extract cell parameters and electron diffraction intensities. Structure solutions were achieved by direct methods using SIR08 [3] and refinement has been performed using SHELX97 [4].

The potential of the method has been demonstrated on several materials of inorganic and organic nature and turned out to be suitable on even highly beam sensitive materials (e.g. pharmaceuticals). Combined with precession technique the quality of the collected intensities allowed us so far to solve crystal structures from crystals of any shape down to 15 nm small particles [5, 6]. Volumes of solved crystal structures reached out to about 4500 Å³ for inorganics and 1500 Å³ for organics. The use of NED made even agglomerated or

embedded samples accessible.

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Keywords: electron diffraction tomography; structure analysis; automation