Incorporating a Preferred Orientation Correction into Supercell Model to Quantify Turbostratically Disordered Nontronite

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Nickel substituted nontronite (~ 2 wt.%) is an important nickel resource in the Western Australian laterite profile. However, the quantitative phase analysis of nontronite has proven to be difficult as this clay mineral is always turbostratically disordered and lacks periodicity in the [00*l*] direction. Therefore a three dimensional unit cell does not exist in turbostratically disordered nontronite and its complex XRD pattern cannot be successfully modelled by conventional Rietveld methods.

Lately, the PONKCS method and its modification [1,2] as well as the supercell approach [3,4,5] were developed to model the diffraction patterns of turbostratically disordered nontronite achieving good accuracy for quantitative phase analysis results. However, the current implementation of the supercell model in the TOPAS symbolic computation system (Bruker® TOPAS v4.2) is not compatible with the preferred orientation macro (March model) which limits its application to XRD patterns without or with low preferred orientation, *e.g.* synchrotron XRD patterns collected in Debye-Scherrer geometry.

A modification of the anisotropic peak scale statement, which is key to the supercell model framework, has been introduced to incorporate the March model correction [6]. This modification enables the supercell model to be used more generally with nontronite XRD patterns that exhibit obvious preferred orientation aberrations, *e.g.* laboratory XRD data collected from front loaded nontronite powder samples. Both the modified supercell model and the previous PONCKS method are applied to XRD data collected on a Bruker® D8 Advance. The quantitative phase abundance results for turbostratically disordered nontronite using both approaches are consistent.

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Estimation of Statistical Uncertainties on Powder Diffraction Data and Pair Distribution Function from 2D Planar X-Ray Detectors

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We describes methods for calculating diffraction intensity and determining their statistical uncertainties in the powder diffraction pattern from data collected with 2D planar detectors, and then propagating the uncertainties of pair distribution function (PDF). In particular, we show the importance of considering the correlation of diffraction intensities during the data reduction. We find that the off-diagonal entries in the variance-covariance (VC) matrix of diffraction intensity come mainly from the pixel splitting algorithm used in many integration steps, for example the default behavior in FIT2D, as well as from the re-binning and re-sampling process. When the full VC matrix can be propagated during the data reduction it is possible to get accurate refined parameters and their uncertainties at the cost of increasing computational complexity. And the accurate VC matrix is the prerequisite of uncertainty estimation in PDF analysis. Since most modeling programs cannot handle the full VC matrix, we explore the best approximate methods for accurately estimating uncertainties from just the diagonal variance terms in the VC matrix.

Crystal Structure of Perovskites as Determined by the Rietveld Refinement for Cathode SOFC

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The room temperature structure of perovskite $L_{1-x} M_x MnO_3$ has been investigated by X-ray powder diffraction and scaning electron microscopy. Rietveld profile analysis of X-ray diffraction data was carried out to determine the symmetry and crystal structures of the $L_{1-x} M_x MnO_3$, where L = La, Fe and M = Sr, Ca, Co; x= 0,55, 0.45, 0,25, 0,20, 0.1. The detailed structural study was analyzed by employing Rietveld refinement techniques with the help of the Topas program, and it reveals the lattice parameters, cell volume, Wyckoff position of the atoms, bond lengths and angles. Also, the crystallite size has been calculated using Rietveld method.

The structure determination of $L_{1-x} M_x MnO_3$ was studied to confirm the electrical conductivity proprieties for cathode function.

Defining Limits for Visual Identification and Quantification of Finasteride Polymorphs by X-Ray Powder Diffraction

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Polymorphism is the property of molecules to crystallize in more than one crystal form, which may affect physicochemical properties. This phenomenon is also present in pharmaceuticals, and evaluation of raw materials to maintain the control of the polymorph present in drugs plays an important role in the pharmaceutical industry. The identification and control of polymorphic forms can be performed using X-ray powder diffraction, and this technique allows characterization of crystalline phases, quantification of amorphous using internal standards and, by means of Rietveld method, refinement of the crystal structure and quantification of phases present in the sample. However, several factors limit the quantification and visual identification of the phases in mixtures, and are related to structure parameters of the sample, such as low symmetry and large unit cell volume, the physical characteristics such as crystallite size and shape, and the resolution of diffractometers which are defined by the geometry, slits, beam monochromatization and detection system. This work presents the visual identification and weight quantification of Active Pharmaceutical Ingredients (API) in binary mixtures samples prepared with two finasteride polymorphs (form I and II) and measured in four different geometries of laboratory diffractometers. Depending of resolution and quality of data, it was possible to identify and quantify polymorphs for percentage as low as 0,5wt%.

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Correction of 2θ Distortions in Powder XRD Patterns Collected on a-Si Flat Panel Detectors

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The use of amorphous silicon flat panel detectors for synchrotron powder diffraction helps enable rapid collection of patterns for in situ studies with good time resolution. However, we have found certain distortions are introduced when using these detectors which are not readily addressed using standard calibration programs such as FIT2D. Radial distortions in patterns collected on these detectors have previously been observed by Lee at al. (J. Synchrotron Rad. (2008). 15, 477-488) for large sample to detector distance (~1778 mm), but corrections for them do not seem to be a well-established part of data reduction procedures at this time.

During our studies of thermal expansion and phase transitions in a variety of materials, we have found quite large discrepancies between the observed and expected peak positions for high angle peaks. To correct these 2θ distortions we have employed a calibration curve obtained from the observed and expected peak positions for a NIST standard LaB_6 sample. LaB6 patterns were collected at various distances between 250 and 600 mm to assess the impact of increasing sample to detector distance on the observed angular distortion. After appropriate calibration and integration, a list of peak positions was generated for each pattern and compared to the peak positions expected based on the wavelength and lattice constant. At 600 mm, only 6 LaB6 peaks were within the usable 2θ range; 25 LaB_6 peaks were within range at 250 mm. A fifth order polynomial correction function was applied to the data to reduce the distortions. Rietveld analysis was conducted on the diffraction patterns before and after applying the 2θ correction to verify that the quality of each fit was improved.

At all sample to detector distances, the peak position errors, |2θ actual-2θ expected|, were reduced dramatically by the correction; at a sample to detector distance of 250 mm, the error in the position of the (520)/(432) reflection is reduced from -0.06° to 0.0008°. Peaks at both low and high 2θ show misfits in the Rietveld analysis: at low 2θ, the fits are skewed to higher 2θ than the actual data; at high 2θ, the fits are skewed to lower 2θ than the data. After correction, the remaining errors no longer appear to be strongly 2θ dependent. This improvement is most pronounced at shorter distances. These results suggest that use of a simple correction function derived from LaB_6 peak positions effectively improves Rietveld fits to powder diffraction data collected with amorphous silicon detectors at short sample-detector distances.

Novel Layered Battery Anode Material $Li_xSn_{3-x}As_2$: Synthesis, Crystal Structure, and Electrochemical Properties

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The development of high-capacity batteries is in great demand for technological applications, such as portable electronic devices and electric vehicles. Current lithium-ion batteries use graphite as the anode material with a maximum capacity of 372 mAh/g. Novel anode materials with higher gravimetric capacities and enhanced charge/discharge capabilities are required for the next generation of batteries. Layered pnictide compounds are promising new anode materials. We report the synthesis, structural and electrochemical characterization of Sn_4As_3 and $Li_xSn_{3-x}As_2$ ($0.6 \leq x \leq 0.8$). The crystal structure of Sn_4As_3 consists of alternating layers of tin and arsenic atoms that are combined into seven-layer blocks that build up along the *c*-axis. Within each block, there is one layer of atoms of each type such that the layer of tin atoms separates the layers of arsenic atoms. The crystal structure of $Li_xSn_{3-x}As_2$ can be described as a derivative of a hypothetical binary tin arsenide, Sn_3As_2. The latter compound has a crystal structure similar to Sn_4As_3 with a reduced thickness of the Sn-As blocks, which are 7 atoms thick in the case of Sn_4As_3 and 5 atoms thick in the case of Sn_3As_2. In the crystal structure of $Li_xSn_{3-x}As_2$ ($0.6 < x < 0.8$), lithium atoms substitute part of the tin atoms in the middle of the Sn_3As_2 block. Thus, lithium is able to partially cut the Sn-As layers apart. Powder X-ray diffraction shows that the unit cell volume decreases with increasing Li content. High-resolution synchrotron X-ray powder diffraction will be used to verify the possible formation of a superstructure arising from the ordering of Sn and Li atoms. We hypothesize that the formation of $Li_xSn_{3-x}As_2$ is the first stage of Li intercalation into Sn_4As_3.

Single Crystal Rotation Electron Diffraction from Multi-phase Powder Samples

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Electron Crystallography is an important technique for studying micro- and nano-sized crystals, too small or too complex to be studied by single crystal or powder X-ray diffraction [1]. Crystals considered as powder by X-ray diffraction behave as single crystals by electron diffraction. Recently we developed a new method, Rotation Electron Diffraction (RED) for three-dimensional diffraction data collection by combining electron beam tilt and goniometer tilt on a transmission electron microscope (TEM) [2]. Here we apply the RED method on an unknown oxide sample in a Ni-Se-Cl-O system, which may show special physical properties, for example magnetic properties.

The crystals in the sample were less than a few micrometers in sizes. Powder X-ray diffraction patterns of the sample could not be indexed by existing known phases. The sample was thus studied by TEM. Three 3D RED datasets were collected from three crystals with different morphologies using the software package RED. Each dataset contained about 1400 frames, with a tilt range of 118-136° and a tilt step of 0.1°. The data processing was also performed using the software package RED-processing, including peak search, intensity extraction, unit cell determination and indexation of reflections. The structures of all three compounds could be solved by direct methods using the program SHELX [3]. One of the structures was later found in the ICSD database and the other two were new. One of the unknown structures was iso-structural to a Co-Se-Cl-O phase which was recently solved by single crystal X-ray diffraction. The coordinates obtained from RED and single crystal X-ray diffraction were very similar. Nearly all peaks in the powder X-ray diffraction pattern could be indexed using these three phases.

In conclusion, three phases from a powder sample have been identified and their structures have been solved by the rotation electron diffraction method. We have shown that RED is a powerful method for structure solution of nano-sized crystals and samples containing multiple phases.

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A Complicated Porous Geramanate framework Structure Solved from X-ray Powder Diffraction

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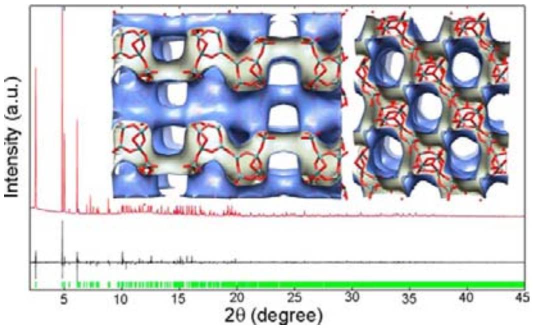
Crystalline micro-porous materials are widely used in industry due to their excellent catalytic, ion-exchange, and adsorption properties. Since these properties strongly depend on the channel system of the framework structure, much effort has been made to explore open-framework materials with novel structures in the past decades. Open-framework germanates are of particular interest for their ability to form diverse structures, especially structures with an extra-large pore. In contrast to silicate based zeolite materials that contain only tetrahedral primary building units, open-framework germanates can be constructed from a variety of Ge-centered coordination polyhedra including Ge-centered tetrahedra, trigonal bipyramids, and octahedra. Combination of these flexible coordination modes of the Ge atom leads to formation of some well-defined clusters which can then be linked to each other by sharing O atoms or through additional primary building units to form a variety of open framework structures with large pores.

As is known, the pore size and channel dimension of a framework structure are crucial factors affecting its application. Those with three-dimensional channels and ring size between 10 and 12 are highly interesting in the catalysis industry. Here, we present GeO-JU90 with a three-dimensional intersecting 12-, 12-, and 11-ring channel system.



Structures of these open-framework materials can be determined routinely by single-crystal X-ray diffraction (SCXRD) if the crystals are big enough. However, in many cases only very fine crystals can be obtained, leaving X-ray powder diffraction (XRPD) and electron crystallography the most promising methods for solving the crystal structure. Due to the sensitivity of germanates under electron beam, electron crystallography could hardly be helpful except for providing unit cell parameters. Therefore, exploring XRPD as a possible technique to reveal the structure for this class of materials is of great importance. Recently, we successfully solved the structure of SU-74 from XRPD data. In this work, GeO-JU90 was determined from the powder charge-flipping algorithm. It contains 11 independent T atoms, which is one of the most complicated germanates solved from XRPD. The guest species in the pores were determined by simulated annealing from XRPD data combining with 13C NMR spectroscopy and other characterization techniques.