MS43-O5 Growth and structural characterization of thin oriented Co_3O_4 (111) films prepared by decomposition of layered cobaltates

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The formation and structure of highly (111)-oriented Co_3O_4 films prepared by a novel procedure from weakly (00l)-oriented NaxCoO$_2$ were studied by XRD. We have found that (111)-oriented Co_3O_4 thin films with (pseudo) epitaxial relation to α-Al_2O_3(001) substrate can by successfully prepared by chemical solution deposition method through the transformation of (001)-oriented NaxCoO2 thin films under optimised annealing conditions. The best results were obtained with the first annealing done at 700 °C for 60 minutes (crystallization of γ-Na_xCoO_2) and the second annealing at 900 °C enabling the transformation of Na_xCoO_2 into Co_3O_4 phase. The degree of preferred orientation in Co_3O_4 as determined by φ-scans and pole figure measurements depended on the Na content in the starting Na_xCoO_2 phase. The content should fall within the region where thermodynamically stable Na_xCoO_2 phases exist (i.e., $0.3 \leq x \leq 1$). The highest volume fraction of well-oriented spinel phase was found for the films prepared from precursor solution with x ~ 0.5. The number of maxima observed in φ scans of spinel phase indicated the existence of in-plane twins since twice more maxima were detected than it would correspond to the multiplicities of the measured lattice planes. Hence the scans suggest the occurrence of two types of growth domains with the same out-of-plane [111] orientation, but with their <011> and <110> axes rotated by 180° into mirror directions. Such twinning is observed for other (hhh)-oriented spinel films on substrates with dissimilar structures. Relatively higher spread (10 °) of in-plane orientation may be a consequence of weaker interfacial bond between film and substrate because the annealing temperatures used were not sufficient to evoke high crystallization and densification of oxidic network. Surface morphology of the films was investigated using electron microscopy and atomic force microscopy. The microstructure of Na_xCoO_2 film was formed by platelet-like grains with the longitudinal size of approximately 500-700 nm. The grains piled up into assembly with pronounced longitudinal texture parallel to the interface. The transformation of (001) oriented Na_xCoO_2 structure into (111)-oriented Co_3O_4 structure manifested itself in change to microstructure of coarse equiaxed grains with the average size comparable to the film thickness and forming near-columnar microstructure. *Supported by the Grant Agency of the Czech Republic no. 14-18392S.*

Keywords: thin films, chemical solution deposition, cobalt oxides

MS44. New applications of old algorithms in crystallography

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MS44-O1 R_{free}: a dinosaur marked for extinction?

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In the early 90s in the absence of rigorous geometric restrains the structure validation was first introduced in the reciprocal space with R-free. Nowadays, however, over fitting can be controlled in real space by the rigorous use of geometric restraints and validation tools. In refinement the practice was established that the deviations from ideal geometry are defined as a target used to scale crystallographic energy terms. Hence, over fitting of models which leads to severe deviations from ideal geometry is not really possible anymore. Hand in hand with the progress of tools delivering better models also the amount of data used for the TEST set was gradually decreasing from the initial 10% and more to 5% and less. Its portion is now practically limited by the request for statistical reliability of the Maximum Likelihood (ML) Cross Validation parameters. The use of the TEST set concept has its limitations: it does not allow the use of all data in refinement and map calculations, the presence of NCS makes it impossible to decouple the independence of TEST set reflections from the rest of the data, and the exchange of the TEST set can result in a considerably different gap between Rwork and Rfree. To overcome the limitations of the Rfree concept we developed an approach that uses the WORK set to calculate the phase error estimates in the ML refinement from simulating the model errors via the random displacement of atomic coordinates. We call it ML Free Kick refinement as it uses the ML formulation of target function and is based on the idea to free the model from the model bias imposed by the chemical energy restrains used in refinement. This approach of calculation of error estimates is superior to the cross validation approach: it reduces the phase error and increases the accuracy of

molecular models, is more robust, provides clearer maps, and may use a smaller portion of data for the TEST set for calculation of the Rfree or leave it out completely.

Praznikar, J. & Turk, D. (2014) Free kick instead of cross-validation in maximum-likelihood refinement of macromolecular crystal structures. Acta Cryst. D70, 3124-3134.

Keywords: refinement, maximum likelihood, Rfree, macromolecule, structure accuracy

MS44-O2 MoPro software: a continual evolution and extension of algorithms from "MOlly for PROteins" to "MOlecular PROperties"

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There have been an increasing number of biological macromolecule structures solved at ultra-high resolution. The refinement program MoPro [1,2] dedicated to the charge density refinement at (sub)atomic resolution of structures ranging from small molecules to biological macromolecules, was therefore developed starting from MOLLY software of Hansen & Coppens [3] written in Fortran language. The program uses the multipolar pseudo-atom model [3] for the electron-density refinement. Alternative methods are also proposed later, such as modelling bonding and lone-pair electron density by virtual spherical atoms.

A charge-density database ELMAM2 [4] was constructed to enable the transfer of multipolar parameters to proteins and was later extended to model common chemical group in organic molecules. The program allows with time more and more complex refinement strategies to be written and has numerous restraints, constraints applying on the charge density or the stereochemistry. Analysis tools to compute the static electron-density and electrostatic potential are derived from the initial MOLLY secondary programs and are available in VMoPro visualisation program. Fourier electron density maps and topological charge integration were programmed from scratch while an existing FFT was incorporated. Some automation tools were programmed to spare the user's time such as local axes definition, importation, exportation, restraints and constraints preparation as well as an automatic charge density refinement strategy.

A graphical user interface MoProGUI was developed in JAVA over the years in order to guide the MoPro user and show him, by exploring the menus, the numerous options and tools available.

The last stage is the development of MoProViewer [5] written in C++, a molecular viewer which is also a Graphical User Interface of VMoPro. MoProViewer enables, in addition, to compute some properties such as the atomic charge in atomic basins from a 3D grid. Some recent tools available are the solvent accessible surface and Hirshfeld surface.

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