

and physical systems [1, 2]. An external stimulus is applied to the system, by periodically varying a parameter affecting it (for example concentration, pH, light flux, temperature or pressure). The response of the system, which is also periodic, is first averaged into one period, then analyzed offline by means of phase-sensitive detection, i.e. by separating the signals of the different frequency terms. A high signal-to-noise ratio is gained by the averaging procedure and the phase-sensitive detection, recovering small signals buried under large ambient noise, besides achieving high time-resolution for kinetic studies [1].

We conceived the application of this technique to Crystallography for two main reasons: to select contributions to the diffraction pattern arising from specific groups of atoms in the crystal cell and to achieve a time-dependent characterization of the crystallized system.

To this aim, we developed a theory to explain the diffraction response of a crystal subjected to a periodically varying external perturbation, where the effect of the variation of different structural parameters on the diffraction intensity is accounted for [3]. We showed that the interference contribution of the substructure composed by the atoms actively responding to the stimulus may be separated by analyzing the diffraction signal at a frequency which is double with respect to that of the external stimulus. This new technique has been called Modulation Enhanced Diffraction (MED).

Experiments to verify the MED potentialities have been first simulated and then carried out at synchrotron sources. The experiments carried out on powder samples, by periodically varying the X-ray beam energy or the pressure exerted by a gas on the sample, will be described.

The data analysis involves two steps: first the phase sensitive detection is applied to a set of diffraction patterns of one modulation cycle to obtain a demodulated pattern, then a phasing procedure is applied to it.

A special procedure, making use of the Patterson deconvolution technique [4], has been developed and successfully used to phase the demodulated diffraction patterns and obtain the substructure of the active moiety.

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Influence of defects on the polarization dependent DAFS of Rutile TiO₂

Matthias Zschornak,^{a,b} Carsten Richter,^{a,c} Dmitri Novikov,^c Sibylle Gemming,^b Dirk C. Meyer,^a ^aInstitute of Experimental Physics, TU Bergakademie Freiberg, (Germany). ^bInstitute of Ion Beam Physics and Materials Research, HZ Dresden-Rossendorf, (Germany). ^cDESY/HASYLAB Hamburg, (Germany). E-mail: matthias.zschornak@physik.tu-freiberg.de

The structural defects of annealed rutile (TiO₂) samples have been studied by means of polarization dependent *Diffraction Anomalous Fine Structure* (DAFS) also known as *Anisotropic Anomalous Scattering* (AAS). The investigations of the ‘forbidden’ 001 and allowed 111 reflection (see Fig. 1) extend the results for the undisturbed rutile structure, space group (136) P4₂/mnm, obtained from AAS by Kirfel and Petcov [1] and from *X-ray Absorption Fine Structure* (XAFS)

analysis (e.g. [2]).

Further, the signature of defects (see e.g. [3]) occurring after thermal treatment at 800°C temperature in a vacuum of about 10⁻⁶ mbar is discussed. An interpretation of changes in the DAFS signal due to electronic transitions into altered unoccupied states is attempted by means of FDM [4] simulations. The considered defects include an oxygen vacancy and a Ti interstitial structure in 2 x 2 x 3 supercells, which in advance have been relaxed using density functional theory. Experiments were performed in the vicinity of the Ti-K absorption edge at DESY/HASYLAB beamlines W1 and E2 on a series of 10 x 10 x 1 mm³ single crystal wafers from Crystec GmbH Berlin.

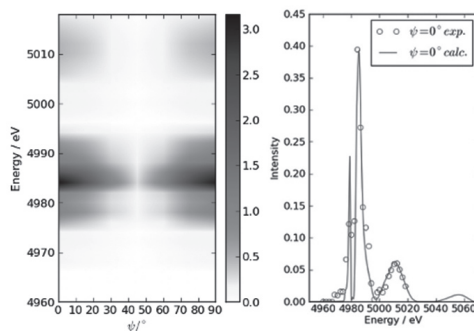


Fig. 1.: Polarization dependent DAFS of 001 forbidden reflection of rutile for σ - π channel (left) and comparison to FDMNES [4] calculation (right).

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Crystal structure and local atomic order in nanostructured La_{0.6}Sr_{0.4}CoO_{3-δ}

Leandro M. Acuña,^a Rodolfo O. Fuentes,^a Diego G. Lamas,^b ^aSolid State Research Center (CINSO-CONICET-CITEDEF), Buenos Aires, (Argentina). ^bCONICET and Facultad de Ingeniería, Universidad Nacional del Comahue, Neuquén, (Argentina). E-mail: acu451@yahoo.com.ar

Mixed ionic-electronic conducting oxides (MIECs) based on transition metal oxides have important application as cathodes in solid oxide fuel cells (SOFCs). The high working temperature of the SOFCs (900 to 1000°C) requires expensive materials to be used as collectors and interconnectors. Start-up and shut-down also reduces the SOFC’s life span due to thermal stresses. So, a great effort is dedicated to the research and development of new cathode materials that exhibit high electro catalytic activity and high ionic conductivity at lower temperature (500-700°C) to be applicable to intermediate temperature SOFCs (IT-SOFCs).

La_{0.6}Sr_{0.4}CoO_{3-δ} (LSC) is one of the best candidates for IT-SOFC cathodes. It exhibits the perovskite-type structure ABO_{3-δ}, where Sr replaces La in the A site, thus introducing oxygen vacancies, which are the responsible for the ionic conduction.

Recently, we have demonstrated that nanostructured LSC cathodes exhibit better electric properties than microstructured ones (area specific resistance, ASR=0.084 and 0.154 ohm cm², respectively). We showed that this high performance is related to the enhanced ionic diffusivity of the nanostructured cathodes [1].