

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

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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.

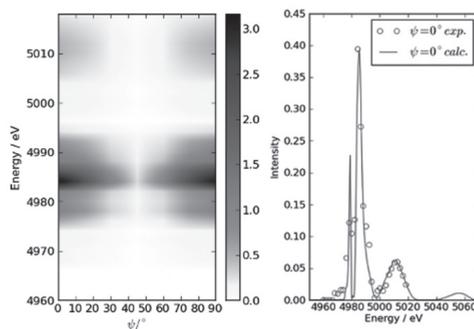


Fig. 1.: Polarization dependent DAFS of 001 forbidden reflection of rutile for σ - π channel (left) and comparison to FDMNES [4] calculation (right).

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

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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].

In the present work, we investigate the influence of crystallite size on the crystal structure, local order and Co oxidation state of LSC nanopowders synthesized by two different chemical methods: citrate-complexation method (C) and stoichiometric nitrate-glycine solution-combustion process (G) [2].

G-process yields porous and deagglomerated powders consisted of nanosized crystallites (average crystallite size, $D = 25$ nm) that exhibit single perovskite phase after calcination at 900°C 5 hours. Citrate complexation method produce foamy powders, but the perovskite phase is achieved at 1100°C . This promotes crystallite growing up to sub-micron sizes ($D > 200$ nm). XRD patterns showed the retention in metastable form at room temperature of the high temperature cubic phase for the nanopowders synthesized by G-process, while powders with bigger crystallite size exhibit the common rhombohedral phase.

X-ray absorption spectra (XAS) of the Co K-edge (7709 eV) were recorded at the D04B-XAFS1 beamline of LNLS, Brazil. Data were collected at room temperature in air. *WinXas* and *fdmnes* codes were used in the analysis. Changes seen in the 2nd derivative of the X-ray absorption near edge spectra (XANES) in the pre-edge region, may be ascribable to the differences observed in the crystal structure and also to oxygen vacancies, as shown by simulations using *fdmnes* code. Also, experimental XANES may be explained in terms of oxygen vacancies. Remarkably, Co(IV) was not needed in these analyses. Some authors claimed Co(IV) appears when Sr substitutes La in LSC [3]. This idea goes against the goal of introduce Sr(II) in the A-site to generate oxygen vacancies, based on unit cell neutrality. Accordingly, Fourier transform of EXAFS signal shows an increase of the concentration of oxygen vacancies in the nanopowdered samples.

In view of the results of this investigation, the enhanced electrochemical performance of nanostructured LSC cathode may be ascribed to a larger concentration of oxygen vacancies, induced by the small crystallite sizes, in the order of 25 nm.

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Structure of an Octahydrated Metformium Decavanadate Salt

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Decavanadate compounds have received considerable attention due to their possible application in blood glucose lowering. The current work is part of a study combining multiple therapeutic agents in the same crystal lattice for potential benefit in treatment of diabetes mellitus. Metformin is a biguanide derivative which is commonly used as an oral hypoglycemic drug to treat type 2 diabetes mellitus. In this study, we report a compound of metformium decavanadate, $[\text{C}_4\text{H}_{12}\text{N}_5^+]_3[\text{H}_3\text{O}^+][\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}] \cdot 8\text{H}_2\text{O}$, synthesized from V_2O_5 , $\text{C}_4\text{H}_{11}\text{N}_5\text{HCl}$, and H_2O in molar ratio of 1.2:1:555 (pH 5) by refluxing at 60°C for 15 hours, followed by crystallization at room temperature. The crystals were analyzed by X-ray diffraction, SEM/EDX, FTIR, and thermal analysis (TGA/DSC) under nitrogen and oxygen atmosphere.

The IR spectrum has a strong peak at 961 cm^{-1} that can be assigned to $\nu(\text{V}=\text{O})$, strong bands at 844 , 743 and 589 cm^{-1} characteristic of $\nu(\text{V}-\text{O})$ and $\delta(\text{V}-\text{O}-\text{V})$, and a weak band at 836 cm^{-1} attributed to

$\nu(\text{V}-\text{OH})$ protonated decavanadate. The bands in the range 3360 - 1067 cm^{-1} are typical of metformium ion. The broad band at 3517 cm^{-1} can be assigned to H_2O in the compound, consistent with eight water molecules corresponding to 9.49% (calc. 9.52%) weight loss observed below 160°C by TGA. An amorphous (by XRD) black residue with weak IR bands at 746 cm^{-1} and 539 cm^{-1} remaining after heating to 700°C was not further characterized. The solution properties of this compound were also characterized using multinuclear NMR spectroscopy.

Keywords: metformium, decavanadate compound, diabetes mellitus

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Ferroelectricity and XANES spectra in PbTiO_3 , BaTiO_3 and SrTiO_3

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PbTiO_3 and BaTiO_3 perovskites have been intensively studied for a long time, because of having ferroelectric (FE) properties at ambient condition and being very useful as functional materials. In particular, some X-ray absorption fine structure (XAFS) studies were carried out to investigate the mechanism of ferroelectric-paraelectric phase transition for these materials [1]. SrTiO_3 has the same perovskite type structure and phase transitions as PbTiO_3 and BaTiO_3 . There is little research of comparing them on detailed temperature dependence and phase transitions. The temperature dependence of Ti-K edge XANES spectrum of PbTiO_3 , BaTiO_3 , and SrTiO_3 perovskite has been investigated. We have investigated the temperature dependence of XANES spectra in order to detail information of local structure on ferroelectric mechanism and distortion of local environments. We performed the synchrotron radiation experiment in the photon factory of KEK in a wide temperature range.

The previous study revealed that [1], in the tetragonal PbTiO_3 and BaTiO_3 phase, a pre-edge absorption has quite large at room temperature. This peak caused by the electronic transition from $1s$ to $3d$ in the Ti atom. The quadrupole transition is enhanced by the addition of a dipole transition from the mixture of p character into the $3d$ final state due to the broken centrosymmetry of the crystal. In the undistorted cubic SrTiO_3 at room temperature, where the structure distortion is minuscule, the feature of pre-edge peaks becomes much smaller but exists. The pre-edge feature is appropriate for obtaining mixture information in $3d \cdot 4p$ orbit of the Ti atom. The feature of the peak of dipole transition and physical properties depend on local structure change in perovskite. In the results obtained in this experiment, the pre-edge feature of ferroelectric perovskite tends to decrease toward Curie point (T_c) with temperature rise. This decrease of this peak is due to the shift from the off-center position of the Ti atom with respect to the oxygen octahedron to center position. The ferroelectric perovskite undergo phase transition above T_c , and it becomes dielectric cubic perovskite. The strong pre-edge absorption has existed and the local distortion remains in cubic phases. The height of pre-edge for dielectric perovskite increases with temperature rise and also from the lowest temperature phase to the highest temperature phase. This increase is not influenced by anharmonic thermal vibration and is thought to be influenced by local distortions by harmonic lattice vibration. It is thought that the tendency that pre-edge absorption of perovskite decreases with temperature rise is only a feature of ferroelectric tetragonal perovskite. By the comparison of XANES