

SLS Symposium on Structure analysis of Novel Materials

Tuesday, August 29, 2017

10:00 to 11:45, WBGB/019

10:00 Deactivation of Fluid Catalytic Cracking Catalysts, a Three-Dimensional View of Structural Changes

Johannes Ihli, R.R. Jacob, M. Holler, M. Guizar Sicairos, A. Diaz, J.C. da Silva, D. Ferreira Sanchez, F. Krumeich, D. Grolimund, M. Taddei, W.-C. Cheng, Y.Y. Shu, A. Menzel, J.A. van Bokhoven

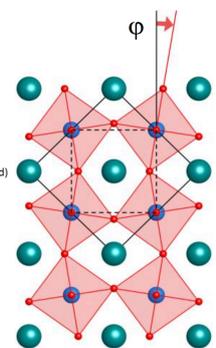
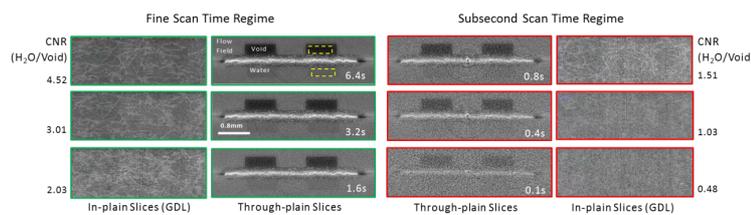
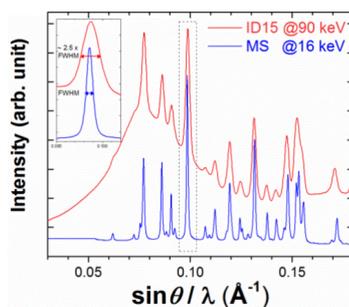
10:30 Fighting the Noise: Towards the Limits of Subsecond X-ray Tomographic Microscopy of PEFC

Hong Xu, M. Bührer, F. Marone, T. J. Schmidt, F. N. Büchi, and J. Eller

11:00 Coffee

11:15 Optically induced transient enhancement of the antiferrodistortive phase in EuTiO₃

Michael Porer, M. Fechner, E. M. Bothschafter, L. Rettig, A. Narayan, M. Radovic, M. Savoini, V. Esposito, J. Rittmann, M. Kubli, T. Kubacka, T. Huber, M. Neugebauer, E. Abreu, S. Grübel, P. Beaud, G. Ingold, G. Lantz, S. Parchenko, S. Song, T. Sato, U. Aschauer, N. Spaldin, S. L. Johnson, U. Staub



Deactivation of Fluid Catalytic Cracking Catalysts, a Three-Dimensional View of Structural Changes

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Since its commercial introduction three-quarters of a century ago, fluid catalytic cracking has been one of the most important conversion processes in the petroleum industry. In this process, porous composites composed of zeolite and clay crack the heavy fractions in crude oil into transportation fuel and petrochemical feedstocks. Yet, over time the catalytic activity of these composite particles decreases. In this talk, we report on resonant ptychographic tomography, diffraction and fluorescence tomography, as well as electron microscopy measurements, which elucidate the structural changes that lead to catalyst deactivation. In combination, these measurements reveal zeolite amorphization and distinct structural changes on the particle exterior as the driving forces behind catalyst deactivation. Amorphization of zeolites, in particular, close to the particle exterior, results in a reduction of catalytic capacity. A concretion of the outermost particle layer into a dense amorphous silica-alumina shell further reduces the mass transport to the active sites within the composite. The results provide a complementary explanation to currently suggested deactivation mechanisms driven by feed and reactor impurities.

Fighting the Noise: Towards the Limits of Subsecond X-ray Tomographic Microscopy of PEFC

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Management and removal of liquid water is essential to maintain and improve the overall performance of polymer electrolyte fuel cells (PEFC). X-ray tomographic microscopy (XTM) of PEFCs has been proven as a valuable tool in order to understand accumulation of liquid water in the gas diffusion layer (GDL), both with in-situ and operando setups. Progress in operando XTM of PEFCs has paved the way for 4D imaging studies of the water distribution in the GDL. In order to capture the water dynamics at high current density operation a further decrease of the scan time towards 0.1 s is aspired. In this work different imaging parameters, filters and their consequences on the contrast-to-noise ratio (CNR) of water versus void and water feature detectability have been studied with an ex-situ XTM experiment at the TOMCAT beamline of the Swiss Light Source (SLS) at Paul Scherrer Institut (PSI).

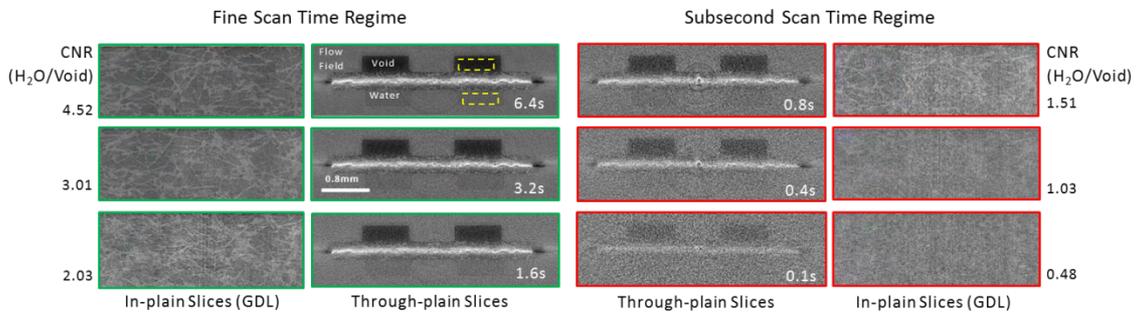


Figure 1: Tomographic in-plane slice and through-plane slice for different tomographic scan times (6.4 s, 3.2 s, 1.6 s, 0.8 s, 0.4 s, 0.1 s) at 13.5 keV; the yellow dashed rectangles indicate the sampling domains for CNR calculation.

Optically induced transient enhancement of the antiferrodistortive phase in EuTiO₃

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Ultrafast optical control of correlation-induced order parameters in complex materials is a key challenge en route to new functional materials. Here we study the ultrafast photoinduced dynamics of an order parameter in a system where phonon-phonon interactions are widely believed to be the primary mechanism of the thermodynamic transition. EuTiO₃ is a perovskite that undergoes a soft-mode-driven [1] structural phase transition at ~280-300K from cubic symmetry (Pm-3m) to tetragonal symmetry (I4/mcm) given by an antiferrodistortive rotation of the oxygen octahedra around the Ti ions (Fig. 1a). We employ above-bandgap femtosecond pulses to excite an EuTiO₃ thin film out of its low-temperature equilibrium phase and monitor the subsequent transient order parameter via intensity of distortion-induced superlattice reflections using 80-fs hard x-ray pulses (at LCLS). We observe a transient increase of the superlattice reflections in a sub-ps time window (Fig. 1b). This represents an optically induced ultrafast increase of the structural order parameter, which stands in contrast to the reduction of the distortion for an increased internal energy in equilibrium. Preliminary DFT calculations suggest 4f-hole-doping in EuTiO₃ as possible driving force. Optically induced enhancement an order parameter has been observed in CDW systems [3,4], but has never been reported for a purely structural distortion, to the best of our knowledge.

We compare this behavior to the results obtained in a similar experiment at FEMTO on SrTiO₃ which is in its relevant aspects similar to EuTiO₃ and exhibits the same type of structurally driven distortion [4]. In striking contrast, we find an initial rapid decrease of the order parameter on a timescale of 0.3 ps. This is much faster than expected for lattice heating from electronic excess energy. The latter we indeed observe as a second, few-ps decay component for both materials.

These results indicate that in systems with phonon-mediated equilibrium phase transitions electronic interactions with the soft mode play a pivotal role in the nonequilibrium case. The possibility to enhance a structural order parameter via optical doping points out a new approach on ultrafast optical control for this class of materials.

[1] D. S. Ellis, et al., Phys. Rev. B, 86, 220301R (2012).

[2] S. Mor, et al., arXiv:1608.05586 (2016)

[3] A. Singer, et al., PRL 117, 056401 (2016).

[4] J. L. Bettis, et al., Phys. Rev. B, 84, 184114 (2011).

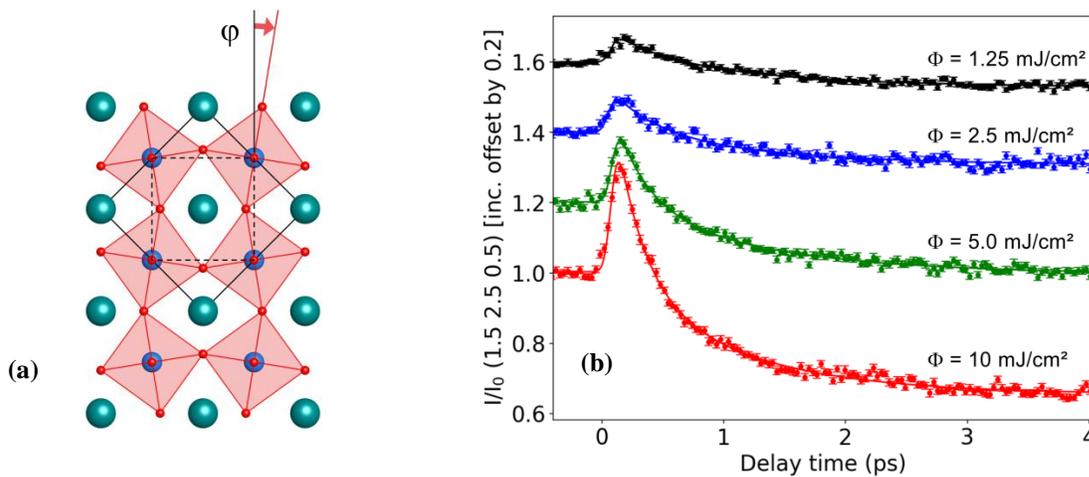


Figure 1: (a) Antiferrodistortive phase of EuTiO₃ and SrTiO₃ as seen along the crystal c-axis. The octahedral rotation angle ϕ defines the order parameter. Green: Eu/Sr; blue: Ti; red: O. (b) Transient x-ray superlattice reflection of an 40 nm EuTiO₃ thin film following photoexcitation with ~40 fs pulses centered around 266 nm measured at $T = 110$ K.