

# SLS Symposium on Dynamics and Kinetics

**Tuesday, February 11, 2014**

**10:00 to 12:15, WBGB/019**

**10:00 Time-resolved (4D) in situ x-ray tomographic microscopy at TOMCAT: Understanding the dynamics of materials during elevated temperature processes**

*Julie L Fife, K. Mader, S. Karagadde, B. Cai, K. Dobson, M. Pistone, R. Pei, K. Yan, S. McDonald, P.D. Lee, P.J. Withers, W.G. Sloof, M. Rappaz, M. Stampanoni*

**10:30 Ultrafast Dynamics in Mixed Valence Manganites**

*Andrin Caviezel, S. O. Mariager, S. L. Johnson, G. Ingold, C. J. Milne, U. Staub and P. Beaud*

**11:00 Coffee**

**11:15 In-situ Spectroscopy of Platinum Catalysts: Identifying the Transient State**

*Urs Hartfelder, J. Singh, M. Nachtegaal and J.A. van Bokhoven*

**11:45 In-situ X-ray Absorption Spectroscopy to study the precipitation of CaCO<sub>3</sub>**

*Sonia Pin and Thomas Huthwelker*

# Time-resolved (4D) in situ x-ray tomographic microscopy at TOMCAT: Understanding the dynamics of materials during elevated temperature processes

Julie L Fife<sup>1</sup>, K. Mader<sup>1,2</sup>, S. Karagadde<sup>3</sup>, B. Cai<sup>3</sup>, K. Dobson<sup>3</sup>, M. Pistone<sup>4</sup>, R. Pei<sup>3</sup>, K. Yan<sup>3</sup>, S. McDonald<sup>3</sup>, P.D. Lee<sup>3</sup>, P.J. Withers<sup>3</sup>, W.G. Sloof<sup>5</sup>, M. Rappaz<sup>6</sup>, M. Stampanoni<sup>1,2</sup>

<sup>1</sup> Swiss Light Source, Paul Scherrer Institut, Villigen PSI, Switzerland

<sup>2</sup> Institute for Biomedical Engineering, ETH - Zurich and University of Zurich, Zurich, Switzerland

<sup>3</sup> Manchester X-ray Imaging Facility, School of Materials, University of Manchester, Manchester, United Kingdom

<sup>4</sup> School of Earth Sciences, University of Bristol, Bristol, United Kingdom

<sup>5</sup> Materials Science and Engineering Department, Delft University of Technology, Delft, The Netherlands

<sup>6</sup> Computational Materials Laboratory, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland

Non-destructive synchrotron-based x-ray tomographic microscopy is ideal for studying various materials systems in three and four dimensions, and the TOMCAT beamline is one of the premier beamlines in the world for such experiments. As examples of recent achievements, 4D directional solidification of dendritic metal microstructures, 4D extrusion of melts in geological materials and 4D self-healing of ceramics have been observed, each for the first time. In such instances, the large amount of acquired data requires the development of *automated* visualization and characterization techniques. This talk will discuss these and other novel results, focusing on the emerging characterization techniques for such systems. For example, the relationship between experimentally determined interface velocity and morphology is examined, as is the use of particle tracking to understand the development of certain phases during the formation of the microstructure. This talk will also highlight proposed instrumentation developments for future research in this area and how such developments will complement the future of the TOMCAT beamline.

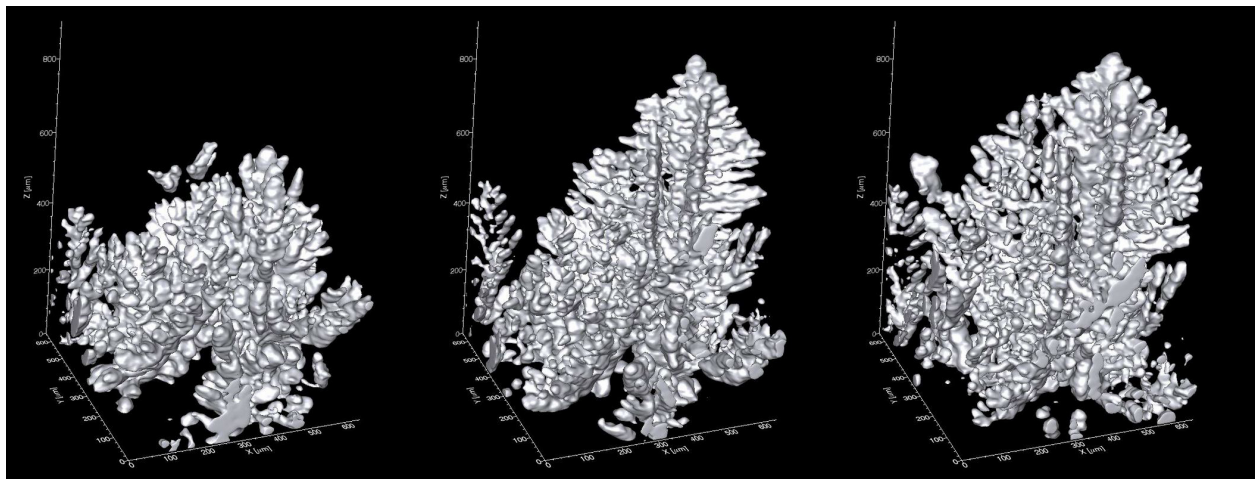


Figure 1. The evolution of Al-rich dendrites in an Al-14wt%Cu sample during time-resolved, in situ directional solidification. Scans were captured continuously for approximately 100s and the elapsed time between the first and last frame shown here is 50s.

# Ultrafast Dynamics in Mixed Valence Manganites

A. Caviezel<sup>1</sup>, S. O. Mariager<sup>1</sup>, S. L. Johnson<sup>2</sup>, G. Ingold<sup>3</sup>, C. J. Milne<sup>3</sup>, U. Staub<sup>1</sup> and P. Beaud<sup>1,3</sup>

<sup>1</sup>Laboratory for Synchrotron Radiation, Swiss Light Source, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

<sup>2</sup>Institute for Quantum Electronics, Physics Department, ETH Zurich, 8093 Zurich, Switzerland

<sup>3</sup>SwissFEL, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

andrin.caviezel@psi.ch

Three dimensional manganites are prototypical examples of strongly correlated electron systems where the complex interactions between different electronic and atomic degrees of freedom manifest in exceedingly rich phase diagrams. The diverse schemes of magnetic, charge and orbital ordering as well as their connection to the structural degree of freedom has been studied extensively in the adiabatic limit. However, comparatively little is known about the interactions among these different degrees of freedom. Investigations in the time domain have the potential to provide new insights on the underlying correlations. It has been demonstrated that phase transformations occurring on a non-thermal time scale can be induced and adiabatically inaccessible, "hidden" states can be activated when exciting the electronic system of these materials with an ultrashort laser pulse. Typically these observations are accompanied by the excitation of coherent optical phonons manifesting the strong coupling between the electronic order and the atomic lattice in these materials.

Here, the focus lies on several members of these 3D manganites, where the Jahn-Teller effect results in a distortion of the oxygen octahedra at the  $Mn^{3+}$  sites and establishes a superlattice along with a CE-type charge and orbital ordering (COO) below the ordering temperature  $T_{COO}$  [1]. Time resolved studies of the laser induced ultrafast melting of the COO phase [2] as well as the advance towards a complete description of the occurring atomic dynamics upon photo-excitation are presented [3,4]. The results reflect not only the progress in the understanding of the involved reaction pathways in this laser-induced phase transition but even more so on the technological developments. The disentangling of the ongoing processes on their relevant time scales bears the possibility to finally exploit the undisputed potential for technological applications of these strongly correlated systems.

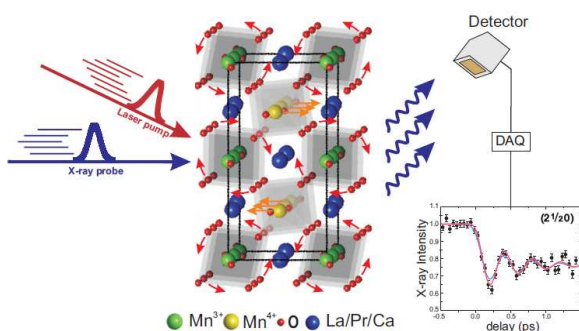


Fig. 1: Schematic of a femtosecond laser pump/x-ray probe experiment

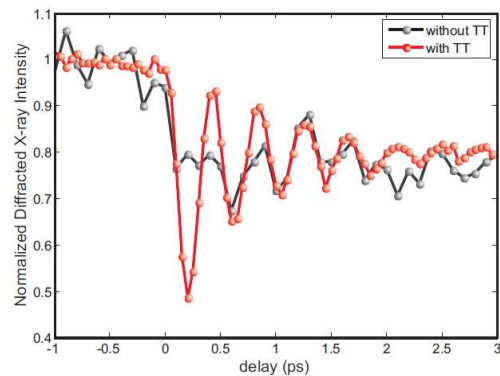


Fig. 2: Single delay scan of PCMO recorded at a FEL with and without laser/x-ray jitter correction

[1] Y. Tokura and N. Nagaosa, Science 288, 462-468 (2000)

[2] P. Beaud *et al.*, Phys. Rev. Lett. 103, 155702 (2009); A. Caviezel *et al.*, Physical Review B 86 174105 (2012)

[3] A. Caviezel *et al.*, Physical Review B 87, 205104 (2013); P. Beaud *et al.*, manuscript in preparation

# *In-situ* Spectroscopy of Platinum Catalysts: Identifying the Transient State

U. Hartfelder, J. Singh, M. Nachtegaal and J.A. van Bokhoven

Carbon monoxide (CO) oxidation over noble metals is a reaction of scientific and practical importance and has been widely investigated by spectroscopic methods. The reaction proceeds in various regimes of different reactivity, depending on the reaction conditions. The typical observed behavior contains a low temperature CO poisoned state and a high temperature state with an oxidic surface. The nature of the surface in the short-lived intermediate phase between these states is subject of strong controversy in the literature.

Using time-resolved XANES spectroscopy at the Pt L<sub>3</sub> edge, we characterized a platinum catalyst during the transition from the CO poisoned to the oxidized state. Principle component and spectral analyses identified the existence of three possible structures. The spectrum of the intermediate phase could be isolated and shown to be that of bare platinum.

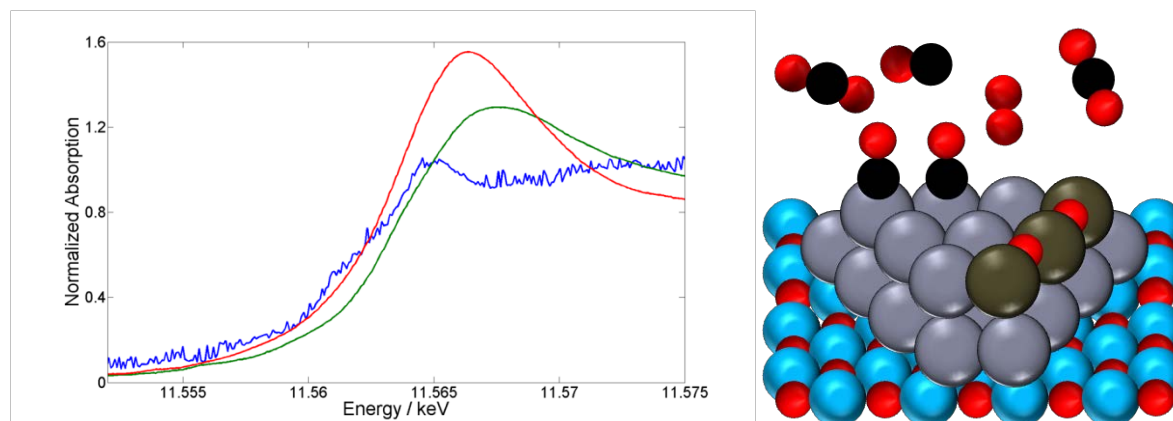


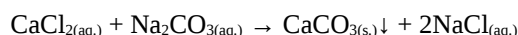
Figure 1: Left: Xanes spectra of CO-covered platinum (green), oxidized platinum (red) and isolated intermediate (blue). Right: Model of a catalyst particle under transient conditions.

# In-situ X-ray Absorption Spectroscopy to study the precipitation of CaCO<sub>3</sub>

Sonia Pin,<sup>a</sup> Thomas Huthwelker<sup>a</sup>

<sup>a</sup> Paul Scherrer Institut, Swiss Light Source (SLS), CH-5232 Villigen PSI, Switzerland. sonia.pin@psi.ch

Calcium carbonate has great scientific relevance in biomineralization and geoscience [1] and provides a model system for classical and nonclassical crystallization theory [2-3]. Despite its relevance, the precipitation mechanism of CaCO<sub>3</sub> is still under intense research and specified complex crystal structures challenge the classical view on nucleation (it exists in at least six crystalline forms), considering the formation of metastable amorphous phase (ACC). In order to understand the mechanism underlying such processes, we want to study the product(s) that forms (form) few milliseconds after the reaction has taken place to get information about the metastable ACC phase. We use a micro-reactive liquid jet to follow *in-situ* the classical reaction of precipitation of CaCO<sub>3</sub>:



An equivalent volumes of the two reactants at the same concentration, at a given temperature, flow-rate and pH are mixed. The final product is studied few millisecond after the reaction is finished than it is collected and measured 1 hour after the mixing. In this contribution, we present a study of the structural and electronic changes in the formed amorphous-CaCO<sub>3</sub> by means of micro-X-ray absorption spectroscopy ( $\mu$ -XAS) at the Ca K-edge in fluorescence mode and X-ray powder diffraction. The XAS features contain information on the local order around Ca and how this is bounded to the near neighbors, showing small but clear changes according to changes in the first shell of Ca, passing from aqueous solution to the metastable phase(s) (Fig.1). The XRPD patterns performed *in-situ* and on the final precipitate give information about the long-range order of the product(s). A preliminary analysis of our recent results measured at the PHOENIX and MS beamlines at the Swiss Light Source will be presented.

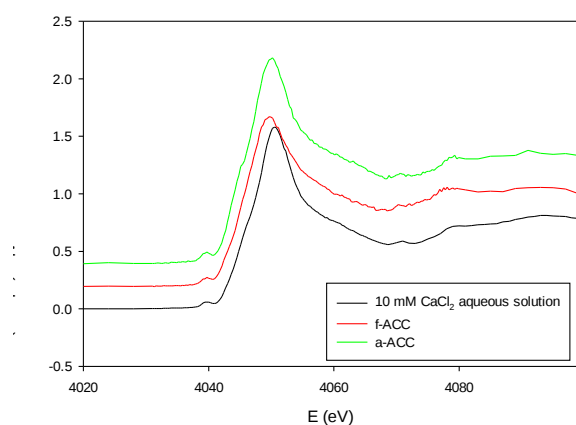


Fig. 1: Normalized Ca-K edge XANES features for the studied reaction in the microliquid reactive jet. Black line: CaCl<sub>2</sub> solution; red line: product formed few millisecond after the mixing; green line: product formed 1 hour after the mixing. Spectra are shifted along the y-axis for better clarity.

[1] R.E. Zeebe et al. *Science* **2008**, 321, 51 [2] J.J. De Yoreo et al. *Rev. Mineral. Geochem.* **2003**, 54, 57 [3] Y. Politti et al. *Adv. Funct. Mat.* **2006**, 16, 1289 [4] J. Rigger et al. *Faraday Discuss.* **2007**, 136, 265