ESRF	**Experiment title:** Real-time x-ray probing of the photoreversible metal to semiconductor transition in a phase-change material Ti3O5	**Experiment number**: HC2849
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Report:

In HC2849 experiment we undertook studies on the photoreversible metal to semiconductor phase transition at room temperature with a unique phase of Ti_3O_5, emerging in a nanocrystalline form [1]. Thermodynamic analysis of this system suggests that the photoinduced metal-semiconductor phase transition results from the laser irradiation of λ-Ti_3O_5, a metastable phase thermodynamically trapped at local energy minimum, to β-Ti_3O_5, a truly stable phase observable on single crystals of the compound. The bulk crystal of Ti_3O_5 is known to exhibit a semiconductor to metal phase transition at high-temperature, around 450 K, associated with a structural symmetry breaking. However, when bulk crystal is downsized to nanoscale (5-50 nm), the case studied in HC2217, a metallic phase with the same symmetry as the semiconductor is stabilized, revealing a very broad temperature range of bi-stability, up to and beyond room temperature. Light irradiation with a strong ns laser pulse causes reversible switching between this trapped metallic state, called λ phase, and the semiconductor state, called β phase [1]. Variable temperature XRD measurements have determined that λ and β belong to the same space group C2/m (monoclinic), but the unit cell parameters vary significantly. For example, λ phase has greater volume than β phase by 6 %. The role of high temperature α-Ti_3O_5 phase (orthorhombic symmetry) remains unclear when the nanocrystalline system is driven out of equilibrium by a pulsed laser.

In HC2849 we built on the experience from HC2217, whereby laser induced signals were collected at the grazing angle geometry: laser exciting from the top, Xrays probing from the side, laser focus tailored to match elongated footprint of Xrays on the sample. The samples of Ti_3O_5 powder were prepared in three forms: (**PF**) pellets of flake powder [1], (**PM**) pellets of SiO_2 matrices [1], and a (**TF**) thin film [2]. The PF contained a majority β nanocrystals (25 nm) forming ~2 μm aggregates, whereas PM and TF contained pure λ nanocrystals (25 nm) but differed by their thickness, 500 nm for TF and 500 μm for PM. Prior to running high excitation experiment to reversibly switch between λ and β, we applied a strategy whereby singular (or majority) phase sample was driven to a transient phase at a low excitation first. That strategy allowed discriminating peak shifts driven by thermal effects from those driven by a phase transition. Unlike in HC2217, in HC2849 we worked with lower energy Xrays, E=11.5 keV. At lower energy we compromise flux for an improved contrast between Xray and laser penetration depth, Fig. 1. In addition to the above improvements over the previous experiment, we opted for a lower repetition rate, 40 Hz down from 1 kHz in HC217.

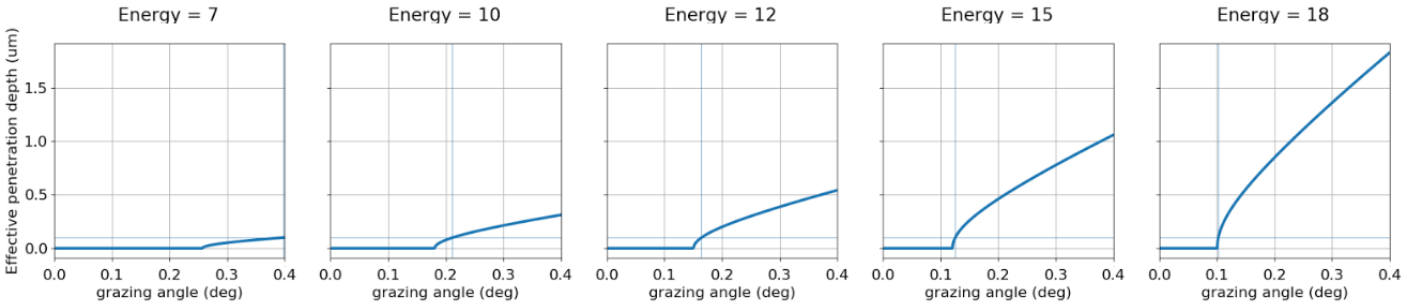

Fig. 1 *Effective penetration depth as a function of incidence angle and Xray photon energy. The estimated laser penetration in Ti_3O_5 is around 100 nm. The incidence angle at which Xray penetrate past the laser penetration mark is illustarted with crosshair. Optimal use of the laser excited volume, as well surface imperfections leading to an ill-defined grazing angle, point to low Xray energies for best signal to noise in the laser pump Xray probe epxeriment. Not shown in the figure, E=11 keV strikes good balance between Xray flux and surface sensitivity.*

This allowed enough time between laser shots to dissipate all heat and recover the true ground state. Not shown in the report, we checked to make sure that scattering patterns at negative delays are identical with those when pump laser is off. In Fig. 2 we show an example of time series on a PF sample. We point to two striking observations while not providing substantiated analysis. First and foremost, due to increased surface sensitivity the time resolved (laser induced) signal is directly observed on the radially integrated absolute scattering signal (upper series of curves). The differential signal, absolute signal at positive delay minus absolute signal at negative delay, provides a view of the laser induced features alone (lower series of curves). Secondly, a preliminary analysis clearly points to the generation of a very strong transient signature, which possibly is a metal of higher symmetry, the α phase. It is noteworthy that around q=2.2 a peak is forming, a (203) reflection in reciprocal space, as would be expected for the α phase. To clarify whether two peaks of the monoclinic symmetry (203) and (-203), become one of the orthorhombic symmetry (203), or the peaks (203) and (-203) move closer upon laser induced heating, or there exists yet another phase, will be aided by a dedicated temperature resolved experiment at the grazing angle (beamtime requested at ID27 or ID15B). Notwithstanding potential future input from such experiments, our ongoing analysis hinges on the entire q range covered in this experiment. The pathway proposed in the literature relies on few selected peaks only [1]. We obtained data of similar quality for **PM** and **TF** samples. Cross correlating the results from those different data sets will help establish whether any new phases have to be considered in the hitherto proposed switching pathway. The high quality data we collected should allow addressing the question whether the suspected threshold excitation density leverages volatile to non-volatile switch, or the mechanisms at low excitation and high excitation are very different.

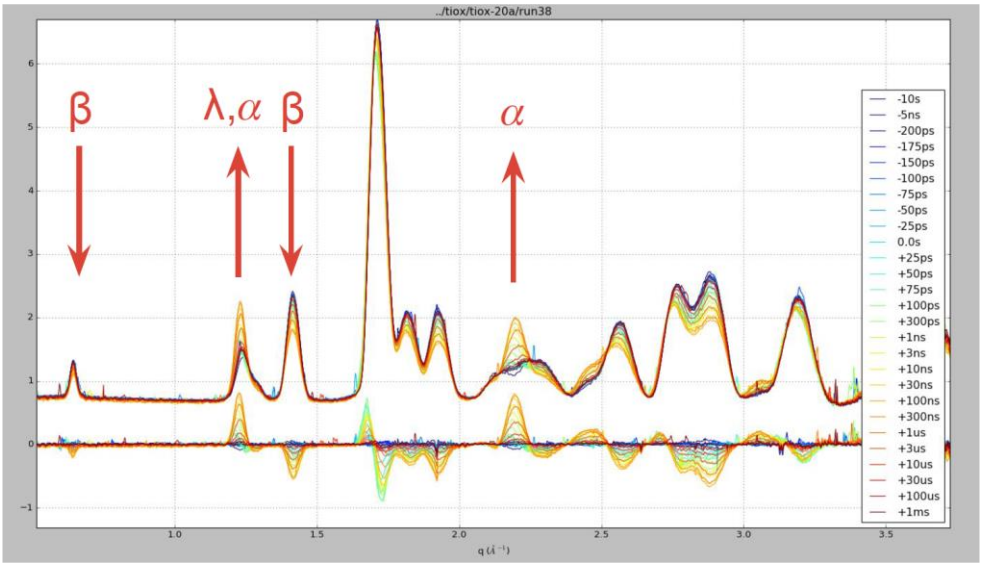

Fig. 2 *Azimuthally integrated differential powder scattering signal for different time delays. Uppers series of curves are the absolute intensities, lower series of curves is the resulting differential signal.*

References

[1] Ohkoshi S. et al., *Synthesis of a Metal Oxide with a Room-Temperature Photoreversible Phase Transition*, Nature Chem. 2, 539 (2010)
[2] Hakoe F. et al., *Dielectric and optical constants of λ-Ti3O5 film measured by spectroscopic ellipsometry*, Materials Letters, 188, 8 (2017)