



Beamline: ID09B	Experiment title: Real-time x-ray probing of the photoreversible metal to semiconductor transition in a phase-change material Ti ₃ O ₅	Experiment number: HC2217
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	Shifts: 12	Local contact(s): Gemma Newby
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Report:

In HC2217 experiment we undertook studies on the photoreversible metal to semiconductor phase transition at room temperature with a unique phase of Ti₃O₅, 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 -Ti₃O₅, a metastable phase thermodynamically trapped at local energy minimum, to β -Ti₃O₅, a truly stable phase observable on single crystals of the compound. The bulk crystal of Ti₃O₅ 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, including 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 -Ti₃O₅ phase (orthorhombic symmetry) remains unclear when the nanocrystalline system is driven out of equilibrium by a pulsed laser.

In HC2217 we were faced a number of experimental challenges, that we prepared in advance to deal with, from sample robustness, to laser excitation, to Xray diffraction geometry. The samples of Ti₃O₅ powder were prepared in two forms: thick pellets (500um) and films (50um) of powder embedded in TEOS for enhanced robustness against laser flux. Knowing the criticality of the phono-induced phenomenon with the laser flux, we opted for an uncompressed amplified beam from ID09's regenerative amplifier running at 800 nm, its optimum mode in terms power delivery, only marginally compromising time resolution (around 200 ps, when compressor is bypassed). Because of a very low penetration depth of the optical excitation in this material, we set up the thick pellet samples in the grazing geometry for incoming X-rays. Thereby, we only collected half of the powder diffraction rings, as the through beam was stopped by the thick pellet, but gained tremendously in terms of S/N for the contrast of photoinduced phase over the bulk phase. In this geometry the footprint of the Xray on the pellet was 60(horizontal) x 1000(vertical) um², with vertical sample slits for incoming Xrays essentially locked to the value 1000 um x grazing_angle, so typically 5 um. The laser beam

was delivered from the top and focused in the plane of the sample with a set of cylindrical lenses, to match the Xray footprint. With films of powder we worked in a conventional geometry, whereby laser and Xray were close to collinear on the sample. Sample slits for Xray were opened to the routine value of 60 x 40 (μm^2) and the laser could be focused much tighter with a spherical lens, increasing the flux by almost a factor of 10 for the same power. The comparison of the two measurements is illustrated in **Fig. 1(a)** and shows unambiguously the advantage of adopting the grazing angle geometry in time-resolved XRD of Ti_3O_5 , and more generally optically opaque solid samples.

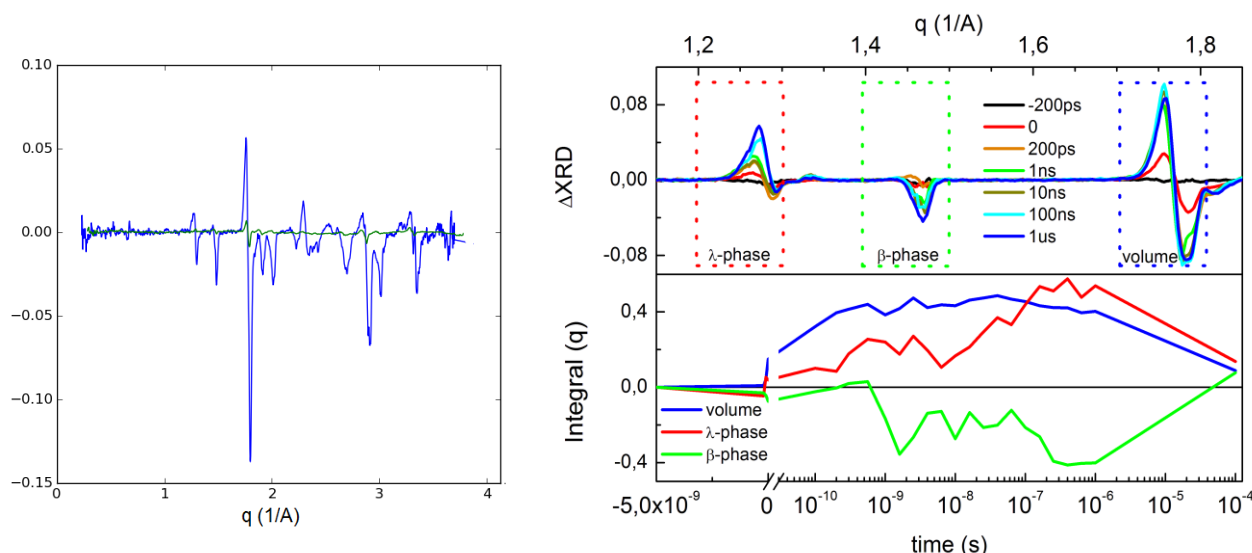


Fig. 1 (a) Azimuthally integrated differential XRD signal at 1 μs delay (1 run average), in the Xray grazing angle experiment (blue), and Xray transmission experiment (green); Note: laser flux 10 times lower in grazing angle experiment; **(b)** Time dependent differential XRD with characteristic peaks for λ ($q=1.3$) and β ($q=1.45$) phases, the common peak ($q=1.75$), as well as time traces showing correlation between phases (red, green integration area) and volume (blue integration area); Volume approximated with a single unit cell parameter.

In another recent study of this material [2], $\beta\text{-Ti}_3\text{O}_5$ phase was excited below that threshold (weak excitation) to the transient $\lambda\text{-Ti}_3\text{O}_5$ phase. Those results, derived from optical spectroscopy, revealed dynamics rationalized in terms of expansion of λ domains on the sub 100 ps time-scale and their shrinking and annihilation on the 100 μs time scale. A very different mechanism, recently evidence by our group [3], points to the coupling between strain-waves and order parameter that can drive and more importantly stabilise the phot-induced phases. Our main objective of HC2217 was to establish whether similar mechanism is at the origin of semiconductor-to-metal transition of the showcased metal oxide. **Fig. 1(b)** is a preliminary analysis of one of the runs in this experiment, with experimental parameters optimised for signal, such as room temperature (RT), laser power (800 μJ). It reveals a strong correlation between the transition from β to λ , and the concomitant unit cell volume change. These changes set in on the sub-nanosecond time-scale, which is the value we expected for propagating at sound velocity the strain waves across nanocrystallites. We carried out series of exactly the same experiments on a number of thick pellet samples, both at RT and 100K, as well as 3 different laser fluencies: weak (200 μJ), moderate (400 μJ), strong (800 μJ). The data we obtained during HC2217 should allow us establish whether the purported mechanism, based on the volume change and the feedback from material, is responsible for the observed transient switching between insulator and metal of Ti_3O_5 . The timespan of accumulated differential signal will also allow distinguish between nonthermal from thermal process, both likely to contribute to the signal. On a longer run, we believe that the new approach, whereby photoinduced signal is collected at the grazing angle, will allow plenty more experiments thus far unsuccessful or not even envisaged because of prohibitive S/N of optically opaque samples.

[1] Ohkoshi S. et al., *Synthesis of a Metal Oxide with a Room-Temperature Photoreversible Phase Transition*, Nature Chem. 2, 539 (2010)

[2] Asahara A. et al., *Ultrafast Dynamics of Photoinduced Semiconductor-to-Metal Transition in the Optical Switching Nano-Oxide Ti_3O_5* , Phys. Rev. B 90, 014303 (2014)

[3] Bertoni R. et al., *Elastically Driven Cooperative Response of a Molecular Material Impacted by a Laser Pulse*, Nature Mater., online DOI: 10.1038/NMAT4606 (2016)