



	Experiment title: Investigating strain wave pathway for insulator-to-metal transition in single crystals : opportunities and bottlenecks	Experiment number: HC4250
Beamline:	Date of experiment: from: 2020.10.27 to: 2020.11.08	Date of report:
Shifts:	Local contact(s): Matteo Levantino, serhane zerdane	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Ritwika Mandal, Institut de Physique de Rennes, CNRS, UM6251 Marco Cammarata, ESRF Céline Mariette, Institut de Physique de Rennes, CNRS, UM6251, remote user (PI) Maciej Lorenc, Institut de Physique de Rennes, CNRS, UM6251, remote user Elzbieta Trzop, Institut de Physique de Rennes, CNRS, UM6251, remote user		

Report:

Goal of the experiment

Recently our group has reported a new pathway to induce ultrafast phase transition in nanocrystalline samples in an efficient and robust manner. This recent work [1] built on time-resolved diffraction measurements, shows how strain waves drive a coherent macroscopic pathway for phase transition from semiconductor (\square) to metal (λ) in bistable Ti_3O_5 nanocrystals, that is associated with a large volume change. It was shown that the phase front starting from the surface propagates in the bulk at sound velocity. This process takes place in an ultrafast timescale (10 -100 ps time scale) and much faster than the heat diffusion (nanosecond). One observation of this study was that the breakdown of the phase front at 100 nm coincided both with the average crystallite size of the nanocrystals and the pump laser penetration, making it difficult to distinguish the limiting factor in this strain wave driven transformation. Here, we were allocated beamtime (**hc4250**) to get new insights into the key parameters affecting the strain wave driven process and multiscale dynamics, including heat diffusion, by investigating the role of crystallite size and pump penetration length.

Measurements performed

For this motive, we performed pump/probe x-ray powder diffraction on titanium pentoxide nanocrystal pellets. The repetition rate was set to 40 Hz to avoid any residual heating effects. We study four different samples, composed of different crystallite sizes, namely 100 nm, 300 nm and 500 nm (figure 1a top to bottom, respectively). For 100 nm crystallite compounds, two different batches were studied with different initial percentages of metallic phase, in order to exclude sample dependent effects. The pellets were excited with a laser beam (pump) from the top, and probed with grazing x-rays at several delays ranging from 50 ps to 1 ms, allowing to probe the “elastic step” (~ 100 ps), the heat diffusion step (# 10 ns depending on samples and fluence) and the full relaxation (within 10 ms). A typical powder pattern obtained is shown in figure 1b (top)

and its time evolution displayed in figure 1b (bottom). This plot reveals sound changes of peak intensities and peak shifts at positive time delays. Several measurements have been performed at different x-ray incident angles to investigate the effect of the depth probed with x-ray. Two different laser wavelengths (400 nm and 800 nm) with different penetration depth were also tried.

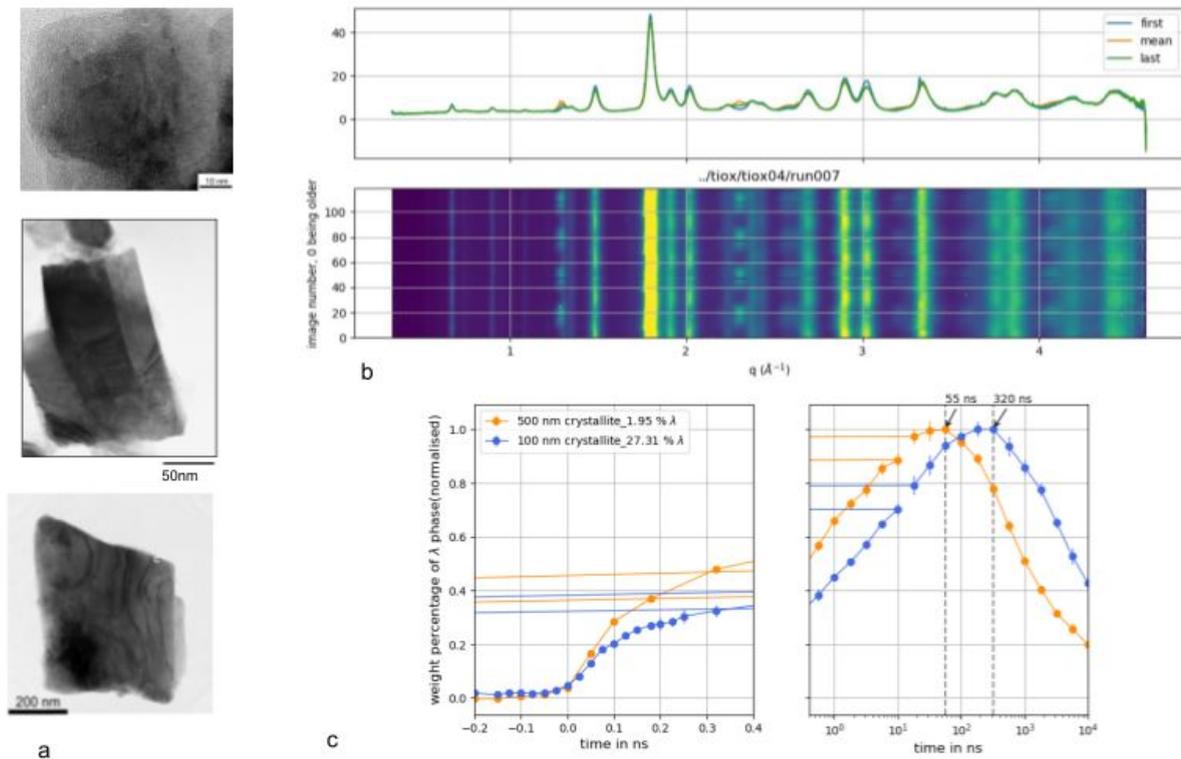


Figure: a) TEM images of Ti₃O₅ nanocrystals from top to bottom [2], [3], [4]. b) Typical 1D powder pattern after azimuthal averaging, bottom: 1D patterns as a function of image number showing the photo-induced changes. c) Change of the metallic (λ) fraction obtained from rietveld analysis of the time resolved powder pattern for 100 nm [2] and 500 nm [4] samples (normalized changes).

Results

Rietveld analysis of all these powder patterns have now been performed and allowed to extract the time evolution of the cell parameter and the fraction of the photoinduced metallic phase. Figure c shows this evolution for two selected datasets for different crystallite sizes (100 nm and 500 nm, same pump fluence and grazing angle). The clear observation is that the relaxation of the heat diffusion takes place much earlier in the 500 nm crystallite sample compared to 100 nm crystallite. The relative amplitude of the transformation in the initial (elastic) step compared with the heating step is also greater for the big crystallites. Further comparisons of different laser power give support for this smallest effect of heat diffusion for bigger crystallites. Power titration, in particular in the infrared regime (little to no energy dissipation per photon absorbed), would however be needed to conclude on this observed size dependance of the strain driven and heat diffusion transformation process.

Problems

Poor X-ray beam stability resulted in significant drifts visible within 20 min - 1 hour (at best). This required frequent realignments making long acquisition difficult and averaging compromised. This also hinders accurate determination of the evolution of the average unit cell distortion, and makes it difficult to make comparisons of absolute signals between different runs.

- [1] Mariette, C., Lorenc, M., Cailleau, H. [...] and M. Cammarata, Strain wave pathway to semiconductor-to-metal transition revealed by time-resolved X-ray powder diffraction. *Nat Commun* 12, 1239 (2021). <https://doi.org/10.1038/s41467-021-21316-y>
 [2] Ohkoshi, Si., Tsunobuchi, Y., Matsuda, T. et al. Synthesis of a metal oxide with a room-temperature photoreversible phase transition. *Nature Chem* 2, 539–545 (2010). <https://doi.org/10.1038/nchem.670>
 [3] Tokoro, H., Yoshikiyo, M., Imoto, K. et al. External stimulation-controllable heat-storage ceramics. *Nat Commun* 6, 7037 (2015). <https://doi.org/10.1038/ncomms8037>
 [4] Ohkoshi, Si., Tokoro, H., Nakagawa, K. et al. Low-pressure-responsive heat-storage ceramics for automobiles. *Sci Rep* 9, 13203 (2019). <https://doi.org/10.1038/s41598-019-49690-0>