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Experimental Report - Beamtime CH-6162 "Studying non-reversible charge-transfer phase transition with time-resolved powder serial crystallography"

Beamline: ID09	**Date of experiment**: 03/11/21 to 09/11/21	**Shifts:** 18
Main proposer: COLLET Eric[1]		**Date of report:** 01/02/2022
Co-participants: CHABAN Ievgeniia[1], HERVE Marius[1], MARIETTE Céline[1], PRIVAULT Gaël[1], ZERDANE Serhane[2] [1] Institut de Physique de Rennes UMR 6251 - Université Rennes 1, France [2] Paul Scherrer Institute, Laboratory for Non-linear Optics (LNO), Villigen, Switzerland		

Experimental purpose of the proposal:

The purpose of the CH-6162 beamtime was to develop a new experimental methodology to perform time-resolved serial crystallography on continuously-refreshed powder, in order to investigate non-reversible photoinduced processes in real time. In particular, Prussian Blue Analogues (PBAs) crystals are known to exhibit thermal hysteresis between two phases: a Low Temperature (LT) phase and a High Temperature (HT) phase, which is accompanied by Charge Transfer (CT) between the two metallic centers (e.g., from Mn^{III}(S=2)-Fe^{II}(S=0) to Mn^{II}(S=3/2)-Fe^{III}(S=1/2) in RbMnFe PBAs). The LT-HT phase transition can be driven by light absorption within the hysteresis, leading to non-reversible and even complete transformation, as demonstrated in a previous beamtime (CH-5458) [1]. While the dynamics associated to the photoinduced CT small-polaron formation was previously measured outside the hysteresis using Time-Resolved X-Ray Diffraction (TR-XRD) [2], the non-reversible character within the hysteresis precluded its dynamical observation through conventional pump-probe techniques on static samples. In addition, when macroscopic phase transition occurs, the lifetime of the excited state is too long to be investigated by pump-probe techniques at 1 kHz repetition rate.

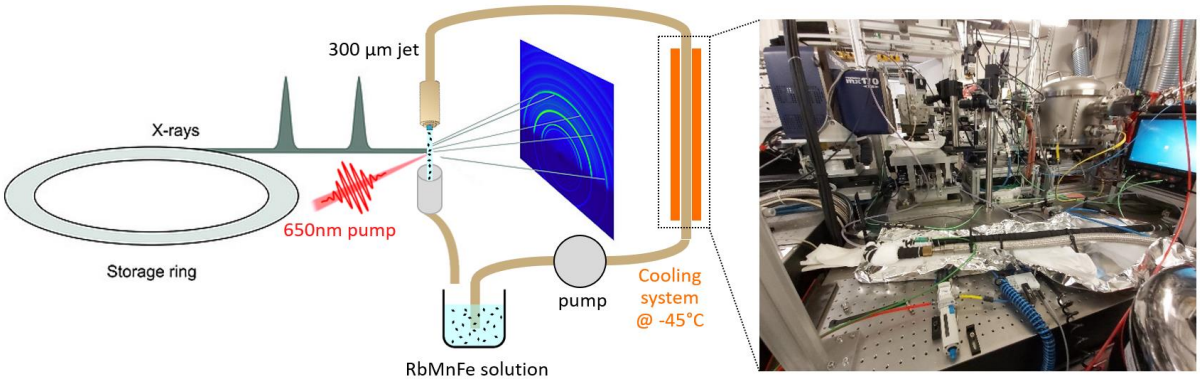

Figure 1. TR-XRD setup used during the beamtime, based on RbMnFe microcrystals dispersed in ethanol and circulating in a closed-loop liquid jet. A picture of the cooling system developed by the Sample Environment Department is shown on the right.

To overcome this limitation, a new interaction configuration was developed in collaboration with ID09 beamline staff and ESRF Sample Environment Department, where PBA microcrystals are dispersed in a continuously flowing liquid jet (see Figure 1). This allowed us to perform TR-XRD measurements on a continuously-refreshed sample, without any limitation by irreversible processes. Additionally, a cooling system was introduced in the closed-loop jet circulation to thermally reverse the phase transition after the photoinduced transformation. We will refer to this new measurement method as "streaming crystallography".

Scientific results of the beamtime:

Using these implementations, we have measured the X-ray diffraction pattern of the dispersed RbMnFe crystals excited by 650 nm light, which induces the non-reversible LT-to-HT transition (Figure 2a). In this way, a fresh (i.e., in the LT phase) ensemble of nanocrystals is excited for each X-ray shot. The evolution of the X-ray diffraction pattern with time gives direct access to the crystal structure and composition after light absorption, and different regimes of dynamics were identified depending on the irradiation fluence. At high fluence, photoconversion from tetragonal LT to cubic HT phases is complete and ultrafast. TR-XRD measurements show that the phase transition occurs within a few hundreds of picoseconds, through a nucleation process. At low fluence, formation of small-polarons is observed as previously measured [2], with local distortions. Additionally, when the photoconversion is not complete within the first hundreds of picoseconds, cooperative effects enhance the conversion rate on the nanosecond and microsecond timescales (Figure 2b). The transition of the crystals is also accompanied with solvent compression, heating and relaxation, which is a signature of the increase in volume of the PBA crystals during the phase transition. Ongoing analysis will solve the structure of the crystals for a greater understanding of the underlying dynamics. The present experiment demonstrates the feasibility to study non-reversible phase transitions with X-ray tools and temporal resolution, and will thus open new opportunities in real-time measurements of processes in materials by using this new streaming crystallography method.

Beamtime issues:

There was no synchrotron radiation at ESRF during the first three days of the beamtime (from 02/11 evening to 06/11 morning), due to vacuum issues in the ring. We thus had only three days left for TR-XRD measurements.

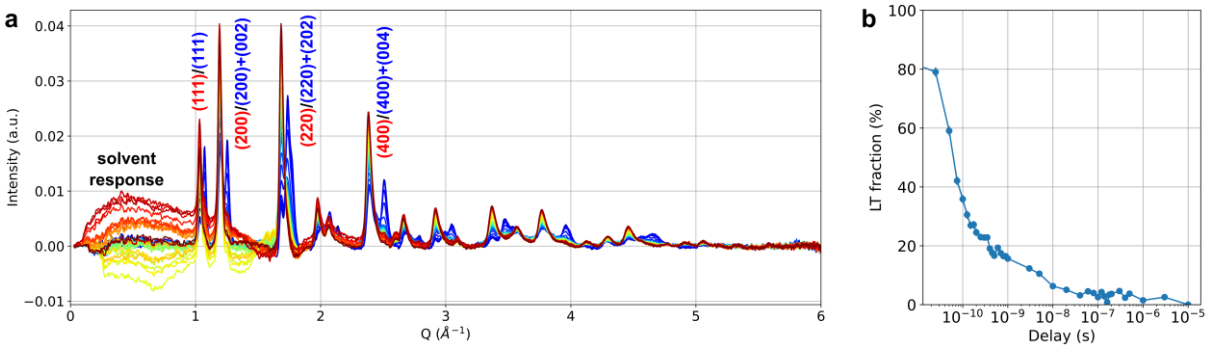

Figure 2. a) TR-XRD pattern of RbMnFe crystals at moderate fluence (0.62 mJ/mm²), from negative delays (-3ns) in blue to positive delays (+10µs) in red. (hkl) indices of the Bragg peaks corresponding to the LT and HT phases are indicated in blue and red respectively. The broad-Q signal (e.g., for Q<1Å^{-1}) corresponds to the solvent response. b) Evolution of the LT phase fraction with delay, showing complete phase transition after ~100ns.

[1] G. Azzolina et al., *Eur J Inorg Chem* **2019**, 3142-3147 (2019).
[2] G. Azzolina et al., *J. Mater. Chem. C* **9**, 6773 (2021).