EUROPEAN SYNCHROTRON RADIATION FACILITY

ESRF User Office
CS 40220, F-38043 GRENOBLE Cedex 9, France
Delivery address: 71 avenue des Martyrs, 38000 GRENOBLE, France
Tel: +33 (0)4 7688 2552; fax: +33 (0)4 7688 2020; email: useroff@esrf.fr; web: http://www.esrf.fr

Experimental Report - Beamtime CH-6492 "Investigating the ultrafast mechanisms of complete and non-reversible photo-induced phase transition in Prussian blue analogues using time-resolved streaming crystallography"

Beamline: ID09	**Date of experiment**: 07/12/22 to 13/12/22	**Shifts:** 18
Main proposer: HERVE Marius[1]		**Date of report:** 24/02/2023
Co-participants: TORRES RAMÍREZ Ricardo Guillermo[1], PRIVAULT Gaël[1], TRZOP Elzbieta[1], GUERIN Laurent[1], COLLET Eric[1] [1] Institut de Physique de Rennes UMR 6251 - Université Rennes 1, France		

Experimental purpose of the proposal:

The purpose of beamtime CH-6492 was to investigate in detail the ultrafast mechanisms occurring during non-reversible photo-induced phase transition (PIPT) within the thermal hysteresis of a class of molecular materials, Prussian blue analogues (PBAs). PBAs are cyano-bridged bimetallic compounds whose general structure is M'(III)-NC-M''(II), and they undergo a phase transition based on a charge transfer between the two metallic sites. In the case of the rubidium manganese hexacyanoferrate ($RbMnFe(CN)_6$) PBA studied here (called RbMnFe thereafter), the electronic charge transfer is coupled with large structural reorganizations, leading to a phase transition with symmetry breaking between a low-temperature (LT) tetragonal phase and a high-temperature (HT) cubic phase. This leads to a broad thermal hysteresis, where the LT-HT phase transformation can be induced by light absorption. In a previous beamtime (CH-6162), we developed a new experimental methodology to study the ultrafast dynamics of the PIPT in RbMnFe, in the specific case of a non-reversible phase transformation within the thermal hysteresis of the compound. This new approach, that we have called *"Streaming Crystallography"*, is based on time-resolved X-ray diffraction (TR-XRD) measurements of RbMnFe micro-crystals dispersed in a continuously-flowing liquid jet. Results from beamtime CH-6162 revealed that PIPT can be complete within less than 1 ns, and leads to a permanent HT phase. However, such a complete transformation occurs only above a laser excitation threshold, whose origin and mechanism remain unclear as many parameters like temperature, excitation wavelength or crystal size can greatly influence the PIPT dynamics.

The scope of beamtime CH-6492 was to investigate the specific role of temperature in the conversion dynamics. According to previous stationary studies [1-3], temperature changes within the hysteresis should result in different final LT-HT conversion rates and therefore different fluence thresholds, but the associated temporal mechanisms were not investigated. To address this question, an important improvement of the Streaming Crystallography setup was undertaken by ESRF Sample Environment Department (Yves Watier) in collaboration with us and ID09 beamline staff: precise temperature control of the liquid jet was developed by introducing a heating system in the jet circulation (Figure 1). This enables to perform TR-XRD measurements of dispersed crystals from -30°C to +70°C, and therefore address the role of temperature in the PIPT dynamics of RbMnFe crystals.

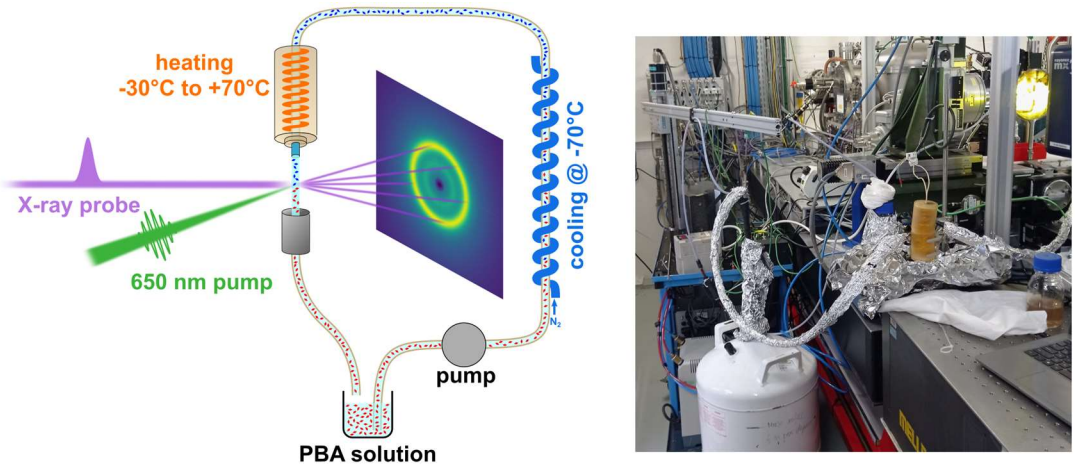

Figure 1. Streaming crystallography setup, that includes a cooling system and a temperature-controlled liquid jet to perform TR-XRD of dispersed RbMnFe microcrystals at various temperatures (a picture is shown on the right).

Scientific results of the beamtime:

Using these new implementations, TR-XRD measurements were done on Co 6%-doped RbMnFe crystals excited by λ=650 nm laser pulses, at different temperatures between -10°C and +20°C (Figure 2). For each temperature, we investigated the ultrafast conversion dynamics from low to high fluence. At low fluence, local formation of small-polarons is observed, that relax back to the initial LT structure within 10 µs [4]. At high fluence, global and non-reversible conversion of the crystals occurs within less than 1 ns. Using temperature control, we measured the temperature and time dependence of the fluence threshold between the local and global conversion regimes. While basic Landau theory suggests a strong temperature dependence [3], our results surprisingly show that conversion dynamics are only gently affected by the temperature of the crystals, keeping the local-to-global threshold fluence similar (Figure 2.b). Ongoing analysis will solve the structure of the crystals for a greater understanding of the role of temperature in the PIPT dynamics, together with deeper analysis using advanced Landau theory. The present experiment demonstrates the feasibility to observe ultrafast dynamics of PIPT within thermal hysteresis, at different temperatures. In particular, temperature control will be very helpful for further studies of compounds whose bistability regime lies outside room temperature (other PBAs, spin-crossover compounds…), therefore opening a broad field of TR-XRD studies using streaming crystallography.

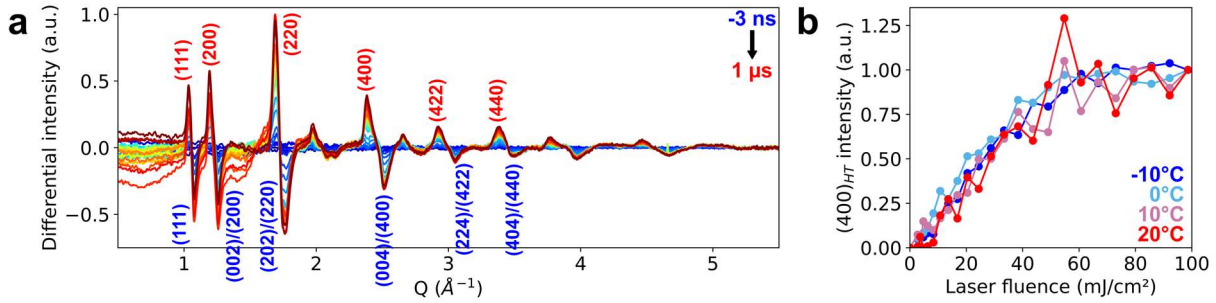

Figure 2. a) TR-XRD differential pattern of Co 6%-doped RbMnFe crystals at moderate fluence (0.62 mJ/mm²) and at -10°C, from negative delays (-3 ns, in blue) to positive delays (+1 µs, in red). (hkl) indices of the Bragg peaks corresponding to the LT and HT phases are indicated in blue and red respectively. b) Fluence dependence of the normalized $(400)_{HT}$ Bragg intensity at +1 ns, for different temperatures (from -10°C to +20°C).

[1] H. Tokoro et al., *J. Magn. Magn. Mater.* **310**, 1422 (2007).
[2] G. Azzolina et al., *Eur. J. Inorg. Chem.* **2019**, 3142-3147 (2019).
[3] G. Azzolina, et al., *Phys. Rev. B* **102**, 134104 (2020).
[4] G. Azzolina et al., *J. Mater. Chem. C* **9**, 6773 (2021).