MS16 Time-resolved diffraction and scattering techniques

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Making ultrafast phase transition movie with streaming crystallography and femtosecond XANES in Prussian blue analogues

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Abstract

The development of modern ultrafast technologies has recently opened new perspectives in controlling bistable materials, where light can be used to switch between different phases and thus different properties [1], by accessing the ultrashort timescales. Specifically, following the dynamics of photo-induced phase switching gives access to the complex couplings between electronic and structural reorganizations, which can be ultimately tuned using ultrafast stimuli. Among the available bistable materials, Prussian Blue Analogues (PBAs) are cyano-bridged bimetallic compounds exhibiting a phase transition based on a charge transfer between two stable states [2]. The electronic charge transfer in these molecular materials is coupled to symmetry-breaking and large volume change, leading to a wide bistability regime [3]. Studying the ultrafast dynamics associated to the photo-induced switching within thermal hysteresis is however hindered by the non-reversible character of the transformation in the bistability range, which is necessary for applications but precludes the use of conventional pump-probe spectroscopy on static material samples. In this work, we overcame this limitation by developing a new Streaming Crystallography methodology, where laser pump – X-ray probe measurements are performed on a continuously-refreshed liquid jet containing micro-crystals in the ground state. We used Time-Resolved X-Ray Diffraction (TR-XRD) at the European Synchrotron Radiation Facility (ESRF) to follow the multiscale phase transition dynamics within the thermal hysteresis of a MnFe PBA driven by optical excitation at 650 nm (Fig. 1) [4,5]. Our results reveal that complete photo-transformation from tetragonal to cubic phase can be achieved in micro-crystals, and leads to a permanent photo-induced phase. The out-of-equilibrium and multiscale dynamical behaviour results from the coupling of volume strain driven by photoinduced charge transfer towards less bonding states and symmetry change related to Bragg peak splitting [5]. More generally, these results open a broad field of dynamical studies for photo-switching resulting in permanent or long-lived states in bistable molecular materials and photo-active devices through ultrafast crystallography.

References

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TR-XRD pattern of MnFe PBA