	Experiment title: Multiferroic-like core-shell particles based on molecular magnets: optimization of the geometry	**Experiment number**: MA-2107
Beamline: ID11	**Date of experiment**: from: 14/05/2014 to: 19/05/2014	**Date of report**: 07/10/2015
Shifts: 12	**Local contact(s)**: Jon WRIGHT, wright@esrf.fr	*Received at ESRF:* 08/10/2015

Names and affiliations of applicants (* indicates experimentalists):

- Dr. Isabelle MAURIN*,
- Dunden Gilang MUHARAM (M2 student)*,
- Tapajyoti DAS GUPTA (PhD student, 2d year)*****,

Laboratoire de Physique de la Matière Condensée, UMR7643, CNRS-Ecole Polytechnique, 91128 Palaiseau Cedex France.

Objective and expected results:

This study is a direct continuation of experiment MA-1821 (April 2013, results published in J. Phys. Chem. C **118** (2014) 13186-13195). The general aim of this project is to investigate photo-induced magnetic switching in heterostructures that associate a magnetostrictive subsystem to a subsystem in which large and reversible striction effects are triggered by light irradiation. We focus on Prussian blue analogues which are able to generate and accommodate large deformations, and which were recently shown to be high-potential candidates for such multiferroic-like architectures based on molecular magnets.[1-3] In the present work, the heterostructures consist of a photoactive core (which lattice expands under illumination) and a magnetic shell.

The MA-1821 experiment has provided direct evidence of a strong retroaction of the shell on the photo-switching properties of the core particles. Indeed, the expansion of the core lattice (and hence the dilation of the core particles) was found to be partly to completely blocked depending on the shell thickness.[4] We could only detect a slight lattice expansion of the core in the case of the 9 nm shell. As a result, we observed only very small modifications of the shell lattice, and small photo-induced magnetization changes in these heterostructures. During the MA-2107 experiment, we have further studied the efficiency of the strain transfer accross the interface in heteroepitaxial core-shell particles of Prussian blue analogues by means of X-ray powder diffraction (XRPD). More specifically, we have investigated the influence of the $Rb_{0.5}Co[Fe(CN)_6]_{0.8}.zH_2O$ (RbCoFe) core size on the photo-switching properties of RbCoFe@KNiCr heterostructures (with a $K_{0.1}Ni[Cr(CN)_6]_{0.7}.z'H_2O$ shell).

Three core sizes were compared: 30 nm, 60 nm and 130 nm and a similar shell thickness of about 15 nm. The distribution of core sizes for each sample is illustrated in Figure 1. All three samples were composed of monocrystalline particles, as evidenced by HRTEM (High-resolution Transmission Electron Microscopy) and confirmed by the analysis of the x-ray diffraction line broadening, with the largest peaks reported for the smaller core particles (see Figure 1). The full diffraction patterns of the corresponding RbCoFe@KNiCr particles are shown in Figure 2. The particles size distributions for the core-shell heterostructures are displayed in Figure 3 (top panel).

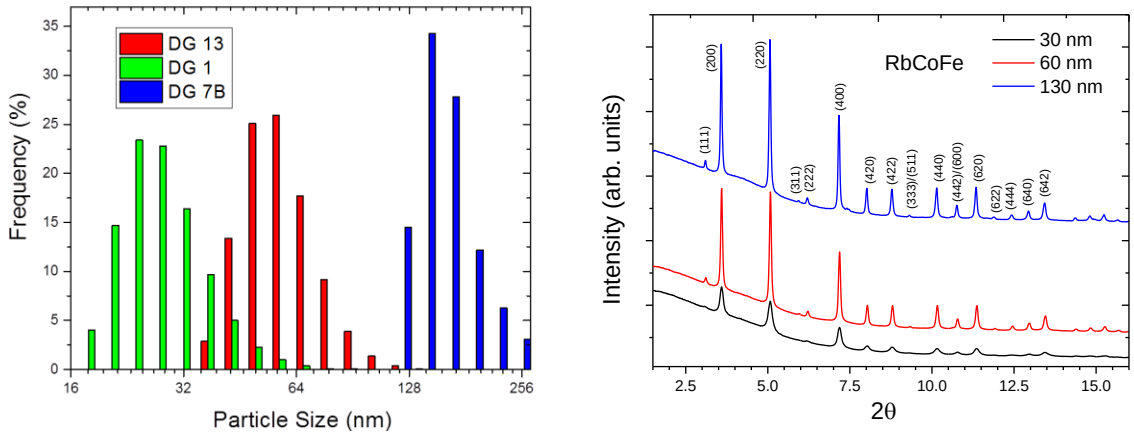

Figure 1: (Left) Distribution of hydrodynamic diameters for the three types of RbCoFe particles determined by Dynamic Light Scattering (DLS). (Right) Synchrotron X-ray diffraction patterns at room temperature of the RbCoFe particles with 30 nm, 60 nm, and 130 nm size (λ= 0.3100 Å, MA-2107).

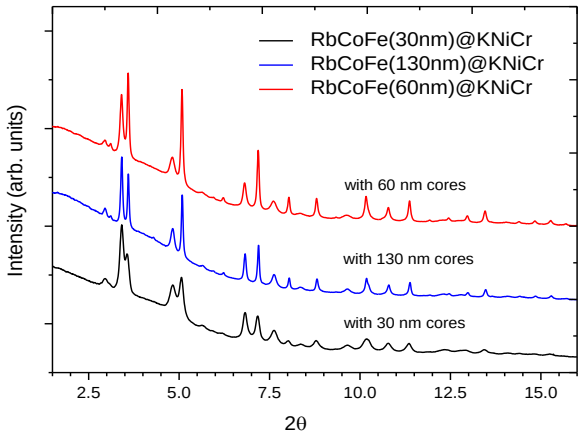

Figure 2: Synchrotron X-ray diffraction patterns at room temperature of RbCoFe@KNiCr core-shell samples with different core sizes (MA-2107).

Experimental method:

To monitor the structural modifications upon light exposure, we used the Helijet unit of the ESRF and a laser diode system (λ= 645 nm, incident power controlled using attenuators). The powder samples were placed in 0.2 mm diameter capillaries and measurements were recorded in Debye-Sherrer geometry using a CCD Frelon camera. Samples were first rapidly cooled down to 100/120 K, then further cooled to 10 K at 2 K/min. Light irradiation was switch on, and then off after reaching a photostationnary state. Additional XRPD data were then collected in the absence of light upon warming up to 120 K (at 2 K/min) to monitor the thermal decay of the light-induced states. This decay temperature is expected to be of the order of 110 K for bare RbCoFe core particles.[4]

The main difficulty that arises during the experiment is related to the cooling system. We suspect large fluctuations of the sample temperature, from one set of measurements to the other, leading to irreproducible or unexpected results. We often reported absence of photo-switching even for bare core particles already measured during the MA-1821 experiment. Tentative trials by increasing the incident laser power were ineffective, as they were inducing some further heating of the sample, eventually leading to irreversible damage. Because of the absence of direct probe of the sample temperature, it required several test experiments to find out the origin of the problem (sample temperature actually higher than 110 K, i.e. the decay temperature of the RbCoFe photo-excited phase). As a consequence, most of the results obtained druing this beamtime session are subject to caution. Hereafter, we only present a selection of these measurements.

Results and conclusion of the study:

In the bottom panel of Figure 3, we show selected diffraction patterns before and during ligth irradiation for bare core particles with 60 nm or 130 nm size (zoom on the (400) Bragg reflections). These observations suggest a large

decrease in the conversion yield of RbCoFe particles when their size is decreased. This finding is likely an artifact due to an insufficient cooling as a full conversion had been reported for 50 nm core particles during the experiment MA-1821.[4] Additional measurements performed during the MA-2511 experiment (April 2015) actually demonstrate that there is almost no dependence of the yield of transformation as a funtion of particle size in the 30 - 130 nm range.

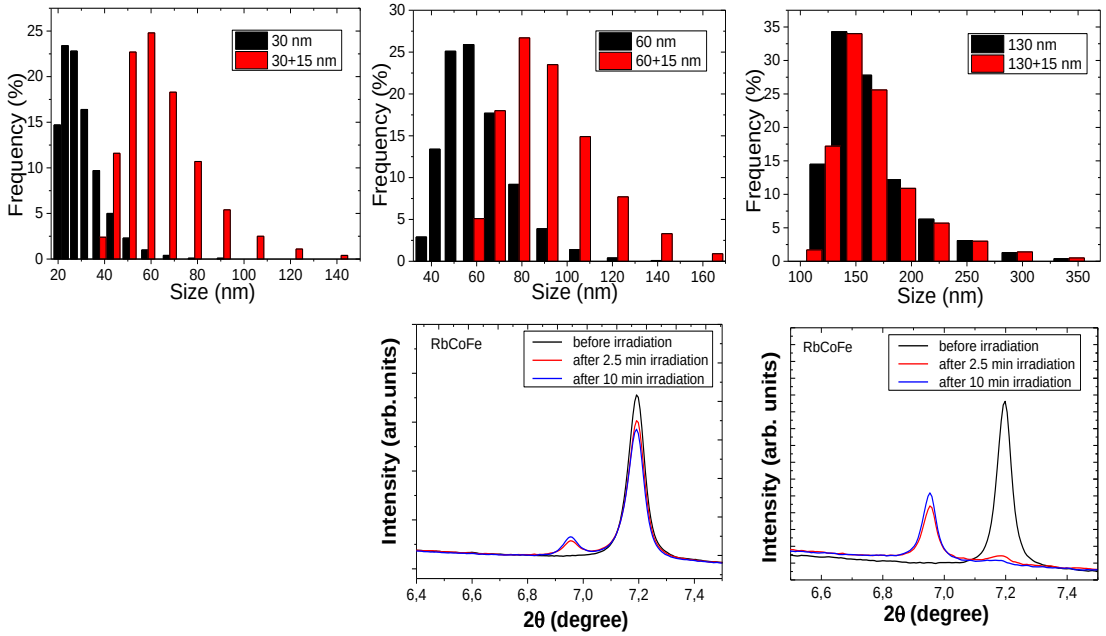

Figure 3: (Top panel) Particle size distribution for the bare core and the core-shell particles from DLS measurements. (Bottom panel) Enlarged view of the (400) Bragg reflections for the RbCoFe core particles with different sizes, and changes as a function of light irradiation. The large decrease in intensity underlight irradiation is ascribed to a movement of the powder in the capillary (direct observation from the video camera).

Similar data were collected for the corresponding core-shell particles and the results are displayed in Figure 4, again with a zoom on the (400) Bragg peaks (low 2θ angle peak: KNiCr shell contribution, high 2θ angle peak: RbCoFe core contribution). This time, we observed that there is a strong dependence of the photo-switching properties of the core particles in the heterostructure as a function of the core size. This finding was confirmed by the MA-2511 experiment. We reach a photo-stationnary state with a large lattice expansion of the core, Δa_{core} = 0.21 Å (and a smowhat smaller expansion for the shell, Δa_{shell} = 0.03 Å) within the first 20 min of irradiation for the biggest 130 nm particles. In contrast, this conversion is almost suppressed for the smallest 30 nm cores. Conversion is only partial for the intermediate 60 nm particles. These different behaviors may be inferred to by a decreased core-to-shell atomic ratio (when the core size is changed from 130 to 30 nm), the shell acting as an optically inactive dead layer analogous to an external pressure preventing the core dilatation. It may also be related to the shell microstructure involving an increased number of shell crystallites (and thus of grain boundaries) for the bigger 130 nm cores, that in turn help accommodating the large dilatation of the core particle as they serve as stress releasing points. Additional measurements were carried out by varying the nature of the shell, but the obtained results may be unreliable and need further confirmation to draw any definite conclusion.

The results of the MA-2107 experiment (room temperature characterizations) and those of the MA-2511 session will be combined in a paper devoted to the influence of the core size and of the core-to-shell atomic ratio on the photo-switching properties of RbCoFe particles in RbCoFe@KNiCr heterostructures.[5] These results should also be supplemented by simulations using continuum or atomistic modeling of the elastic interactions.

Justification about the use of beam time:

The 15 shifts have been used as follows:
- 2 shifts to set up the sample environment (helijet unit and irradiation system) and align the beam,
- 1 shift for room temperature characterizations,
- 10 shifts using sequences of measurements as the one described in the experimental method. Test experiments were performed to understand the absence of photo-induced structural changes in most of the investigated samples: laser

power, temperature, comparison with previously measured samples. We conclude to a problem of temperature regulation (probably large fluctuations of the sample temperature),

- finally, 2 shifts were used with some stability of the temperature regulation. Measurements were restricted to kinetics of photo-switching at 10 K and characterization of the steady states in the absence of light. We studied RbCoFe@KNiCr core-shell particles with different core-sizes, the corresponding bare cores and three samples with different shell compositions.

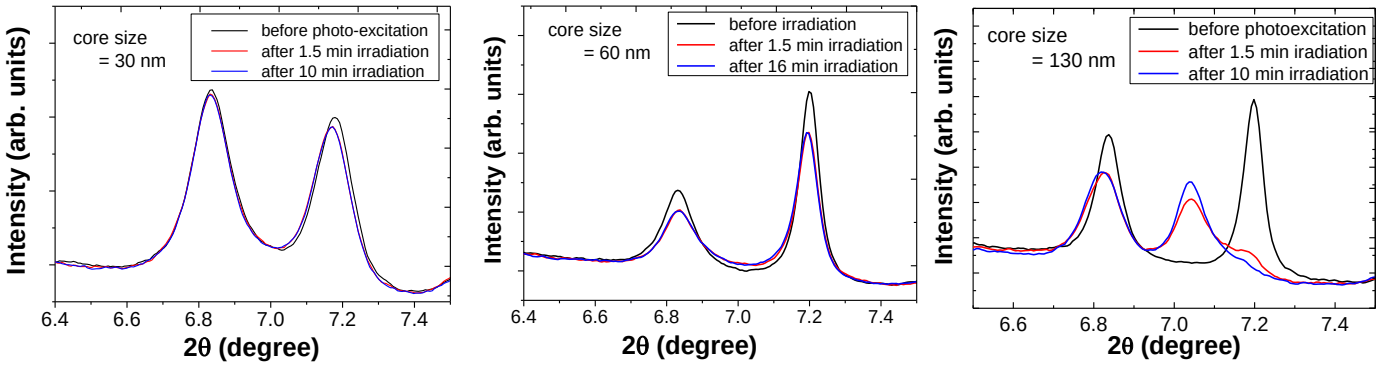

Figure 4: Enlarged view of the (400) Bragg reflections RbCoFe@KNiCr core-shell samples with different core sizes, and changes as a function of light irradiation.

---

[1] Pajerowski *et al.*, J. Amer. Chem. Soc. 2010, **132**, 4058.
[2] Dumont *et al.*, Inorg. Chem. 2011, **50**, 4295.
[3] Risset *et al.*, DOI: 10.1021/acs.chemmater.5b02785.
[4] Presle *et al.*, J. Phys. Chem. B 2014, **118**, 13186.
[5] Adam, in preparation.