



	Experiment title: Multiferroic-like heterostructures based on molecular magnets	Experiment number: MA-1821
Beamline: ID11	Date of experiment: from: 05/04/2013 to: 09/04/2013	Date of report: 19/08/2014
Shifts: 12	Local contact(s): Jon WRIGHT, wright@esrf.fr	<i>Received at ESRF:</i> 19/08/2014
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Photostrictive/Piezomagnetic Core-shell Particles Based on Prussian Blue Analogues: Evidence for Confinement Effects?

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ABSTRACT: High-quality core-shell particles, which associate a photostrictive core ($\text{Rb}_{0.5}\text{Co}[\text{Fe}(\text{CN})_6]_{0.8} \cdot z\text{H}_2\text{O}$, **RbCoFe**) and a ferromagnetic shell ($\text{Rb}_{0.2}\text{Ni}[\text{Cr}(\text{CN})_6]_{0.7} \cdot z'\text{H}_2\text{O}$, **RbNiCr**), were successfully grown by a multi-step protocol based on coprecipitation in water.

High-resolution transmission electron microscopy shows that well defined heterostructures are formed and that the core/shell interface is abrupt with the epitaxial relationship $001\mathbf{RbCoFe} // 001\mathbf{RbNiCr}$, confirmed by simulations of the x-ray diffraction linewidths. The core particles are monocrystalline, with 50 nm sides, and the shell consists of large platelet-like crystallites, with a height that corresponds to the shell thickness and lateral dimensions comparable to the size of the core particles. Analysis of the diffracted intensities as a function of shell thickness (9-26 nm) shows that the epitaxial shell growth does not lead to a thick pseudomorphic layer at the interface. In contrast, Williamson-Hall plots suggest that a structural relaxation takes place to adapt the mismatched lattices, with the formation of misfit dislocations distributed over the entire shell thickness. This later finding is indicative of an effective mechanical coupling within the heterostructures. However, a magnetization increase by only a few percent was observed under light irradiation for these $\mathbf{RbCoFe@RbNiCr}$ particles. We showed from in-situ synchrotron x-ray diffraction measurements that these small changes most likely reflect confinement effects as photoswitching of the core phase is partly or completely blocked depending on the shell thickness.

in J. Phys. Chem. C **118** (2014) 13186-13195.