Polyhedron 123 (2017) 323–327

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Pressure-tuning of the photomagnetic response of heterostructured CoFe@CrCr-PBA core@shell nanoparticles

Marcus K. Peprah [a], Derrick VanGennep [a], Pedro A. Quintero [a], Oliva N. Risset [b], Tatiana V. Brinzari [a], Carissa H. Li [b], Matthieu F. Dumont [a], Jian-sheng Xia [a], James J. Hamlin [a], Daniel R. Talham [b,*], Mark W. Meisel [a,*]

[a] Department of Physics and National High Magnetic Field Laboratory, University of Florida, Gainesville, FL 32611-8440, USA
[b] Department of Chemistry, University of Florida, Gainesville, FL 32611-7200, USA

ARTICLE INFO

Article history:
Received 8 September 2016
Accepted 30 November 2016
Available online 16 December 2016

Keywords:
Core–shell nanoparticles
Heterostructures
Prussian blue analogues
Photomagnetism
High pressure

ABSTRACT

Using a home-made, anvil pressure-cell mounted to a probe suitable for use with a commercial magnetometer, the photo and thermal responses of the magnetism of CoFe@CrCr-PBA (PBA = Prussian blue analogue) core@shell nanoparticles were studied down to 5 K and up to 0.5 GPa in 100 G. The effect of pressure on the magnetic ordering temperatures of the CoFe-PBA core (≈25 K) and the CrCr-PBA shell (≈200 K) along with a shift of the relaxation temperature of the photo-CTIST (charge-transfer-induced spin-transition) of the CoFe-PBA core (≈125 K), were similar to the behaviors reported for the single-phase materials. Specifically, although the magnetic ordering temperature of the CrCr-PBA shell shifted to higher temperatures, the relaxation temperature of the photo-CTIST of the CoFe-PBA core moved to lower temperatures when the pressure was increased, thereby lowering the temperature range under which the CrCr-PBA component can be photoswitched.

1. Introduction

By their nature, molecule-based magnetic systems are significantly "softer" than their solid-state counterparts. Consequently, external pressure and strain are being widely applied to coordination polymers and single-molecule magnets to probe a range of emerging multiferroic behavior [1–7]. An important coordination polymer family are the Prussian blue analogues, which are cubic cyanide-bridged mixed-metal networks of general formula $A_jM_k[M'(CN)_6]_l \cdot nH_2O$, where the monovalent ion A is located in the intersticies, as needed, to balance charge. The shorthand MM′-PBA can be used to indicate an analogue of two first-row transition metals, M and M′. Recently, photocontrol of the magnetic response in CoFe@CrCr-PBA core@shell nanoparticles has been demonstrated to persist to 125 K [8]. In this system, the persistent, photoinduced changes of magnetism of the heterostructure are compromised by the thermal relaxation of the structural changes associated with the photo-CTIST (charge-transfer-induced spin-transition) effect of the CoFe-PBA core, since the light-induced phase transition of the core couples to the shell whose magnetic response is modified.

This investigation of CoFe@CrCr-PBA core@shell nanoparticles evolved from studies of CoFe@NiCr-PBA hetrostructures (thin films and nanoparticles) in which the photocontrol of the magnetic response of the NiCr-PBA component was observed up to its ordering temperature, $T_c = 70$ K [9,10], as the light-induced state of the CoFe-PBA core persists to even higher temperature. In contrast, although photocontrol of the magnetic response of CoFe-PBA@CrCr-PBA is observed to higher temperature, up to 125 K, which is the relaxation temperature of the metastable light-induced state of the core, the magnetic changes do not persist up to $T_c = 200$ K, the ferrimagnetic transition temperature of the CrCr-PBA shell. The motivation for the present study was to see if the photoinduced magnetic changes could be shifted by external pressure from 125 K to 200 K. Specifically, a home-made, anvil pressure-cell suitable for use with a commercial magnetometer was used to investigate the photo and thermal responses of the low-field magnetic response of CoFe@CrCr-PBA core@shell nanoparticles, whose ambient pressure response has been reported elsewhere [8].

Using PBA heterostructures, a series of comprehensive studies by several groups have elucidated the robust magneto-mechanical coupling at the interface of the two components and the interplay

* Corresponding authors.
E-mail addresses: talham@chem.ufl.edu (D.R. Talham), meisel@phys.ufl.edu (M.W. Meisel).

http://dx.doi.org/10.1016/j.poly.2016.11.046
0277-5387/

between the size of the cores and the thicknesses of the shells for observing photoinduced changes in the magnetic response [11–14]. Although the effect of external pressure on the magnetic behavior of several PBAs has been reported, including CoFe-PBA [15–18] and CrCr-PBA [19] that are the components of the system used in present study, the magnetic changes induced by light and pressure have not been previously reported for PBA heterostructures. Herein, the observed effects of pressure on the magnetic ordering temperatures of the CoFe-PBA core ($T_{N,c} \approx 25$ K)[1] and the CrCr-PBA shell ($T_{N,s} \approx 200$ K), along with the shift of the temperature where the photo-CTIST of the CoFe-PBA core relaxes ($T_R \approx 125$ K), are similar to the behaviors reported for the single-phase materials [18,15,16,19]. In other words, although the $T_{N,s}$ of the CrCr-PBA shell shifted to higher temperatures, the T_R of the CoFe-PBA core moved to lower temperatures when the pressure was increased. These results provide a guide for future approaches seeking to observe photocontrolled magnetic response at higher temperatures in these kinds of heterostructures, and chemical tuning of the CoFe constituent will play a significant role [20,21,17].

2. Experimental methods

2.1. Sample synthesis and characterization

The core@shell nanoparticles of $\{Rb_{0.2}Co[Fe(CN)_6]_{0.7}\}_{0.8}$@ $\{K_{0.1}Cr[Cr(CN)_6]_{0.7}\}_{0.2} \cdot 4H_2O$ (CoFe@CrCr-PBA) used for this study were from the same batch of material whose synthesis protocols and structural properties were described elsewhere [8,22]. The cubic cores of CoFe-PBA have sides of 172 ± 13 nm, whereas the CrCr-PBA shell has a thickness of 9 ± 2 nm. Attempts to grow thicker CrCr-PBA shells on the CoFe-PBA core seed particles resulted in the nucleation of pure CrCr-PBA particles, so the present sample represents the thickest CrCr-PBA shell grown to date. The sample used in this pressure study had a mass of approximately 4.0 μg.

2.2. Anvil pressure cell

The homemade optical-access pressure cell for use with a commercial magnetometer follows closely the miniature anvil cell described by Giriat et al. [23] and is based on the Tozer turnbuckle design [24]. A complete set of schematics and detailed drawings are available elsewhere and online [18]. A CuTi alloy was used as the primary component of the cell because of its low magnetization properties. The main cell body consists of an octagonal prism that measures 7 mm in length and 7 mm in diameter. Four 1 mm diameter holes are placed on four flat sides of the cell body and serve as viewing windows for the culets and the gasket. In addition, the cell consists of two pressurization screws (6 mm in diameter and 3 mm in length) that are counter threaded to provide the turnbuckle mechanism. Atop the screws, three machined holes form a triangle, and a fourth hole (1 mm) at the center provides access for an optical fiber when irradiating the sample space. The application of pressure is delivered by silicon carbide (SiC) anvils, whose culet diameter was 800 μm. A BeCu gasket with a 290 μm hole confined the sample, a small Ruby (Al_2O_3 with Cr^{3+} doping) whose fluorescence served as the manometer by following established protocols [25,26], and a tiny amount Daphne-7373 oil employed as the pressure transmitting fluid [27–31]. The fluorescence spectra were acquired by a home-made, inexpensive mini-spectrometer [32], which provided excitation at 405 nm. The resulting emission at 694.3 nm was used to provide pressure measurements at all temperatures ($2\ \text{K} \leqslant T \leqslant 300$ K). During the final assembly stages an optical microscope was used to position the anvils, and a defect was noticed at the edge of one of the anvils. This defect restricted the present work to pressures $P \leqslant 0.5$ GPa, while the minimum pressure value, typically $P \approx 0.05$ GPa, is needed to insure a snug (leak-tight) fit of the anvils to the gasket. It is noteworthy that a pressure of 0.5 GPa has a significant effect on the magnetic and photomagnetic response of single-component CoFe-PBA [15,16,18], and examples of this response [18] are provided in the Supplementary Material (SM), which is available online. In addition, the temperature dependence of the magnetic signal arising from the cell sans sample is provided in the SM.

2.3. Protocols for measuring the magnetic response

To avoid quenching the thermal-CTIST transition of the CoFe-PBA component [33] and straining the single optical fiber (with a 600 μm diameter active optical core and an overall outer diameter of 720 μm) extending from room temperature down to the sample cell, the cooling rates were restricted to $\leqslant 3$ K/min down to 100 K and then to $\leqslant 5$ K/min at lower temperatures. Similarly, warming rates were limited to $\leqslant 2$ K/min for $T \leqslant 10$ K and 5 K/min for $10\ \text{K} < T \leqslant 300$ K. The cooling/warming/measuring processes were always in the presence of a static, applied magnetic field of 100 G.

The dark state data were acquired with a black cover on the room temperature end of the optical fiber. The light state was achieved at 5 K by irradiating the sample with unfiltered light generated by a halogen bulb after waiting for nominally 1 h before starting the irradiation process, which typically lasted about 2 h. When the light was switched off and the fiber was covered, the sample remained at 5 K for another hour before the warming process was initiated. Typical plots of the magnetic response as a function of time are shown in the SM section.

3. Results and data analysis

The temperature dependences of the magnetic susceptibility $\chi = M/B$, where M is the magnetization and $B = 100$ G, are shown for the dark and light states at pressures $P = 0.05$ GPa (essentially ambient pressure) and 0.5 GPa, Fig. 1. The background signal from the pressure cell has not been subtracted. An effective means to judge the photoinduced changes is to plot the differences between the light and dark states, namely $\Delta\chi = \chi(\text{Light}) - \chi(\text{Dark})$. This type of analysis allows for a simple and efficient method of eliminating the background signals arising from the pressure cell as these magnetic signals do not possess a photoactive response. In addition, the changes at low temperature, $T \lesssim 25$ K, dominate the subtle changes at higher temperatures, $25\ \text{K} \lesssim T < 300$ K, so these regimes are plotted separately in Figs. 2 and 3.

Although the $\Delta\chi$ data sets are weak and somewhat noisy for $T \gtrsim 25$ K, Fig. 3(a), it is important to note these changes in the magnetic response of the core@shell particle arise from the distortion of the magnetic domains of the CrCr-PBA shell in response to structural changes associated with the light-induced CTIST in the CoFe-PBA core. Furthermore, the high-temperature response of the system is detectable because of the distortion of the magnetic domains in the CrCr-PBA shell [8]. The overall photoinduced changes persist up to $T_R \approx 125$ K, which is temperature where the thermal relaxation of the photo-CTIST of the CoFe-PBA core occurs. At this temperature, the photoinduced lattice anisotropy is nulled, so the distortion of the magnetic domains in the CrCr-PBA shell assume their thermal equilibrium arrangements. From Fig. 3(a), the data do not clearly resolve the effect of external pressure on the temperature regions of $T_R \approx 125$ K and $T_{N,s} \approx 200$ K, the ferrimagnetic transition of the CrCr-PBA shell [8]. Conse-

[1] The Néel temperatures of the PBA constituents of the core and shell are designated as $T_{N,c}$ and $T_{N,s}$, respectively.