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**RESEARCH
HIGHLIGHTS**



**EVENTS AND
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OTHER NEWS

NEWSLETTER 2018



Dear Colleagues and friends,

2018 has been the first year of the Indian-French Laboratory of Solid State Chemistry² IFLaSC² in English or LaFICS² in French is an Associated International Laboratory created in 2003 between the Centre National de la Recherche Scientifique (CNRS), a French public scientific and technological institution, the Université de Caen Basse Normandie (UCBN), the Université de Strasbourg (US), public scientific and professional institutions and The Indian Institute of Science, Bangalore (IISc), an autonomous public institution funded by the government of India which were at this occasion happy to welcome a new partner the Université de Bordeaux (UB). Several laboratories and institutions linked to the CNRS, the UCBN, US and UB and the IISc are involved in this LaFICS² that are:

- the Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB)
- the Centre de Recherche Paul Pascal (CRPP)
- the Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS)
- the Laboratoire de Cristallographie et Science des Matériaux de Caen (CRISMAT)
- the Ecole Nationale Supérieure d'Ingénieurs de Caen
- The Solid State and Structural Chemistry Unit, (SSCU), IISc, in Bangalore
- Materials Research Center (MRC), IISc, in Bangalore
- The Indian Institute of Technology, Bombay, India (IIT/B), through its Department of Metallurgical Engineering & Materials Science (MEMS)



- The Indian Institute of Technology, Madras, India (IIT/M), through its Department of Chemistry

With this News Letter and in collaboration with my homologue in India, Prof. Satish Patil, I wish to bring some more dynamism to this LIA and encourage Indians and French Researchers to promote excellent and fruitful collaborative projects.

In this News Letter you will then find some insights concerning the activities performed in the framework of this LIA.

Enjoy your reading!

Marie Helene DELVILLE, PhD

Research highlights

Halappa, P.; Mathur, A.; Delville, M. H.; Shivakumara, C., Alkali Metal Ion Co-Doped Eu^{3+} Activated GdPO_4 Phosphors: Structure and Photoluminescence Properties. *Journal of Alloys and Compounds* 2018, 740, 1086-1098. 10.1016/j.jallcom.2018.01.087

ICMCB, France/IISc Bangalore, India

Series of alkali metal ion co-doped with Eu^{3+} activated GdPO_4 phosphors were synthesized by the conventional solid state method. Structural parameters were confirmed by the X-ray Rietveld refinement method. All the compounds are crystallized in the monazite phase with space group $(P12(1)/n(1), \text{No.14})$. Morphology and functional group analysis were performed on scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR). Room temperature photoluminescence (PL) spectroscopic results reveal that, on Eu^{3+} ion doping in the GdPO_4 host matrix, the magnetic dipole transition ($^5\text{D}_0 \rightarrow ^7\text{F}_1$) at 581 nm responsible for orange light, dominates the red emission with respect to the electric dipole transition ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) at 620 nm. It was found that the emission intensity increased up to 9 mol% of Eu^{3+} and then quenched due to multipolar interactions. Further, co-doping with Li^+ , Na^+ and K^+ ion in to Eu^{3+} activated GdPO_4 phosphor led to an enhancement in luminescence intensity by reducing the parity restriction of electric dipole transitions as a consequence of suitable local distortion of the crystal field surrounding the Eu^{3+} activator ion. The results of Judd–Ofelt theory and radiative parameters suggest that these phosphors have a short lifetime, good quantum efficiency, excellent color purity compared to other reported Eu^{3+} doped phosphors. These results illustrate the mechanistic effect of alkali metal ions doping on luminescent properties of rare earth ion doped GdPO_4 phosphors and help in optimization of their luminescent properties according to the practical requirements in optoelectronic and biomedical applications.

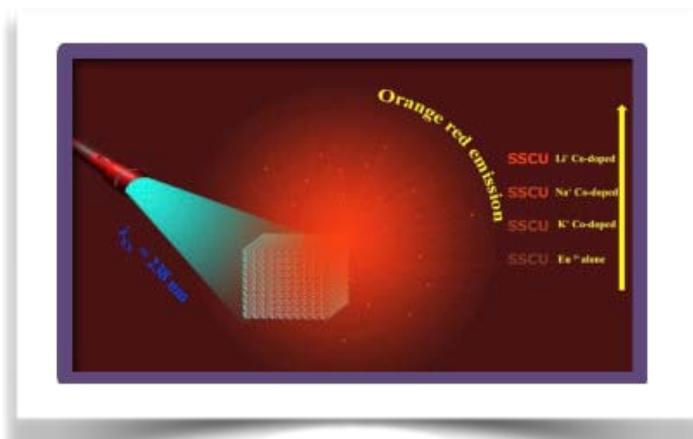
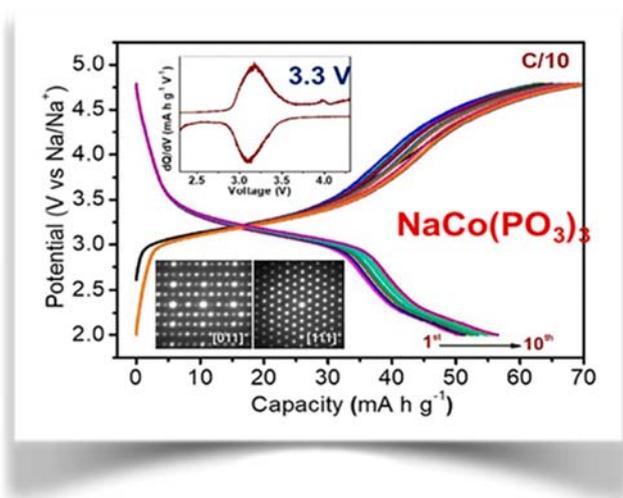


Figure (a) Bright field low resolution TEM images and corresponding ED rings, (b) EDX elemental mapping and (c) bright field HRTEM image of Co–Ni nanoparticles

Gond, R.; Rao, R. P.; Pralong, V.; Lebedev, O. I.; Adams, S.; Barpanda, P., Cubic Sodium Cobalt Metaphosphate $[\text{NaCo}(\text{PO}_3)_3]$ as a Cathode Material for Sodium Ion Batteries. *Inorg. Chem.* 2018, 57, 6324-6332. 10.1021/acs.inorgchem.8b00291

IISc Bangalore, India /CRISMAT, France

The authors synthesized and characterized Cubic-framework sodium cobalt-based metaphosphate $\text{NaCo}(\text{PO}_3)_3$ was recently demonstrated to be an attractive Na^+ cationic conductor. It can be potentially used in the next-generation rechargeable Na ion batteries. The crystal structure and elec. cond. were studied and found to have a three-dimensional framework with interconnecting tunnels for Na^+ migration. This inspired us to study the electrochem. (de)intercalation behavior of Na^+ in the $\text{NaCo}(\text{PO}_3)_3$ assuming a cubic $\text{Pa}\bar{3}$ framework. Herein, synergizing exptl. and computational tools, we present the first report on the electrochem. activity and Na^+ diffusion pathway anal. of cubic $\text{NaCo}(\text{PO}_3)_3$ prepd. via conventional solid-state route. The electrochem. analyses reveal $\text{NaCo}(\text{PO}_3)_3$ to be an active sodium insertion material with well-defined reversible $\text{Co}^{3+}/\text{Co}^{2+}$ redox activity centered at 3.3 V (vs Na/Na^+). Involving a solid-soln. redox mechanism, close to 0.7 Na^+ per formula unit can be reversibly extd. This exptl. finding is augmented with bond valence site energy (BVSE) modeling to clarify Na^+ migration in cubic $\text{NaCo}(\text{PO}_3)_3$. BVSE analyses suggest feasible Na^+ migration with moderate energy barrier of 0.68 eV. Cubic $\text{NaCo}(\text{PO}_3)_3$ forms a 3.3 V sodium insertion material.



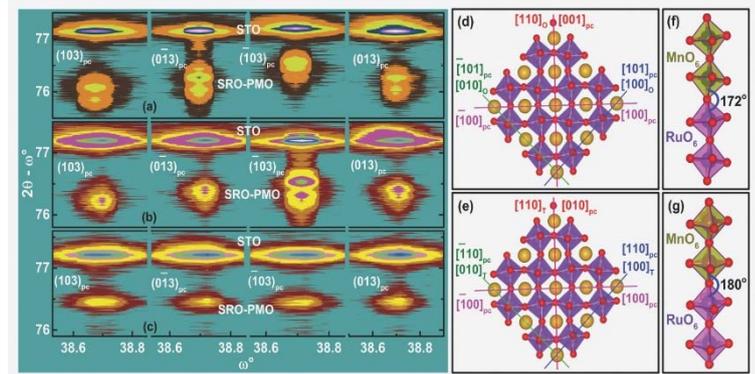
Sahoo, A.; Prellier, W.; Padhan, P., Effect of Symmetry Breaking on Interlayer Exchange Coupling and Electrical Conduction in SrRuO_3 – PrMnO_3 Superlattices. *Advanced Materials Interfaces* 2018, 5, 1800913 doi:10.1002/admi.201800913

IIT Madras India/CRISMAT, France

The breaking of orthorhombic to tetragonal crystal symmetry is realized by increasing the PrMnO_3 layer thickness in the superlattices consisting two ferromagnets, SrRuO_3 and PrMnO_3 . The octahedral rotation pattern is $a^+c^-c^-$ and $a^0a^0c^-$ type for the superlattices with orthorhombic and tetragonal phase, respectively, inferred in the simulated projected density of states. The 15% reduction in d_{z^2} orbital occupancy due to the $a^0a^0c^-$ type octahedral rotation compared to that of the $a^+c^-c^-$ type suggests the presence of stronger antiferromagnetic (AFM) coupling. The larger orbital overlapping leads to a stronger spin–orbit coupling, associated with a shift of 42.8% of the minor in-plane field cooled (FC) magnetic hysteresis loop ($M(H)$) along the magnetization axis in orthorhombic superlattices. While, minor in-plane FC $M(H)$ shifts along the field axis due to the strong AFM coupling in tetragonal superlattices. In field-dependent magnetoresistance, the rotation of spins in the antiferromagnetically coupled interfacial layers is detected as a unique anomaly, which is stronger in the superlattices for the biased spins and tetragonal symmetry than the pinned spins and orthorhombic symmetry. The results demonstrate that the tuning of interfacial exchange coupling and spin-

dependent transport by controlling structural distortion could be used as a tool in fabricating modern spintronics-based devices.

Figure. Reciprocal-space-mapping around $\{103\}_{pc}$ planes of $(001)STO/[17 \text{ u.c. SrRuO}_3/n \text{ u.c. PrMnO}_3]_{15}$ superlattices with a) $n = 1$, b) $n = 2$, and c) $n = 3$. Schematic representation of the atomic arrangements in the d) $(101)_{pc}$ of superlattices with $n = 1$ or 2 and e) $(110)_{pc}$ of superlattices with $n = 3$ or 4. Schematic representation of the MnO_6 and RuO_6 octahedra at the interfaces along the $[001]_{pc}$ of superlattices with f) $n = 1$ or 2



Pal, A.; Sekhar, C. D.; Venimadhav, A.; Prellier, W.; Murugavel, P., Investigations on the defect dipole induced pyroelectric current in multiferroic $GdMnO_3$ system. *Journal of Applied Physics* 2018, 123, 014102. [10.1063/1.5001245](https://doi.org/10.1063/1.5001245).

IIT Madras India/CRISMAT, France

Pyroelectric current measurements on the orthorhombic $GdMnO_3$ polycrystalline sample are done to explore the intrinsic and extrinsic contributions. The measurements reveal poling temperature dependent pyrocurrent peaks at 20, 50 and 108 K. The pyrocurrent at 20 K and at 108 K are attributed to ferroelectric transition induced by the incommensurate spiral magnetic ordering of Mn spins and the release of trapped charges from the localized states, respectively. A detailed analysis on the broad pyrocurrent signal at 50 K suggests that it could be attributed to the thermally stimulated depolarization current effect due to the relaxation of defect dipoles induced by negatively charged Mn^{3+} ions and excess holes localized at Mn^{4+} sites. Importantly, the effect of the electric field due to the defect dipoles on the ferroelectric state is highlighted. The temperature dependent dielectric measurements under the magnetic field brought out the correlation between pyroelectric and dielectric properties. The influence of poling temperature dependent extrinsic effects on pyrocurrent suggests the

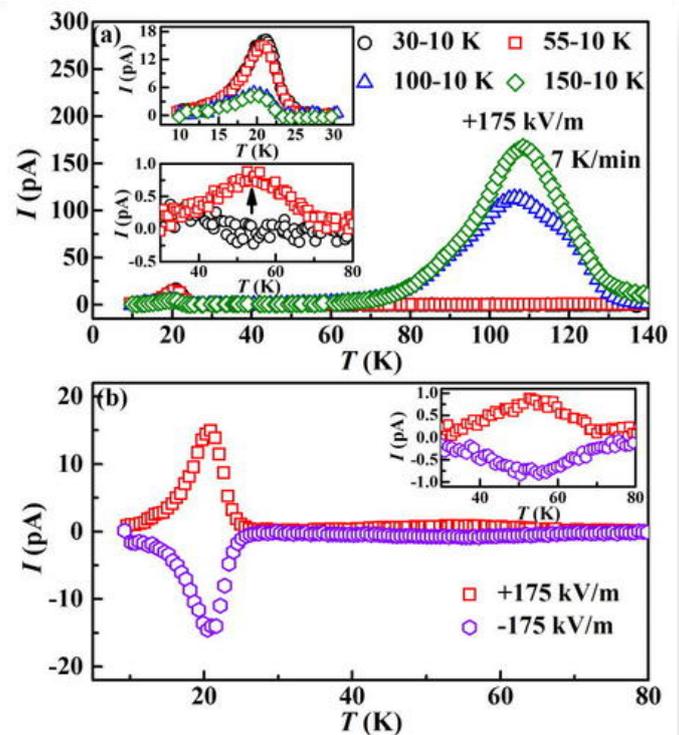


Figure (a) Pyroelectric current is plotted as a function of temperature for different poling states under +175 kV/m poling field. The upper and lower insets show the corresponding plots near the ferroelectric transition and a

choice of poling temperature on the study of polarization and the resultant multiferroicity in a spin-driven ferroelectric rare earth manganite system.

Chakrabarty, A.; Raffy, G.; Maity, M.; Gartzia-Rivero, L.; Marre, S.; Aymonier, C.; Maitra, U.; Del Guerso, A., Nanofiber-Directed Anisotropic Self-Assembly of CdSe-CdS Quantum Rods for Linearly Polarized Light Emission Evidenced by Quantum Rod Orientation Microscopy. *Small* 2018, 14, 1802311. 10.1002/smll.201802311
ICMCB, France/IISc Bangalore, India

Hybrid soft materials composed of CdSe-CdS nanorods or "quantum rods" (QRs) and the fluorescent 2,3-didecyloxyanthracene (DDOA) low molecular weight organogelator are obtained through self-assembly. Spectroscopy, microscopy, and rheology studies show that the QRs and DDOA coassemble, thereby stabilizing the organogels. Depending on the QR load and excitation wavelength, single nanofibers (NFs) of the hybrid gel display either sharp polarized red luminescence (under green excitation), or dual perpendicularly polarized blue and red emissions (under UV excitation). Transmission electron microscopy, microspectroscopy, and quantum rod orientation microscopy (QROM) reveal that QRs align along the organogel NFs with order parameters reaching 76% and 87%. This paves the way for obtaining surfaces of QR/NF assemblies yielding sharp red linearly polarized emission. In addition, this work demonstrates that QRs can be used more generally to probe nanostructured soft materials, even nonemissive ones. QROM allows to establish maps of the orientation of single QRs dispersed onto or within a gel network by measuring the polarization of the emission of the individual QRs. As occurs within

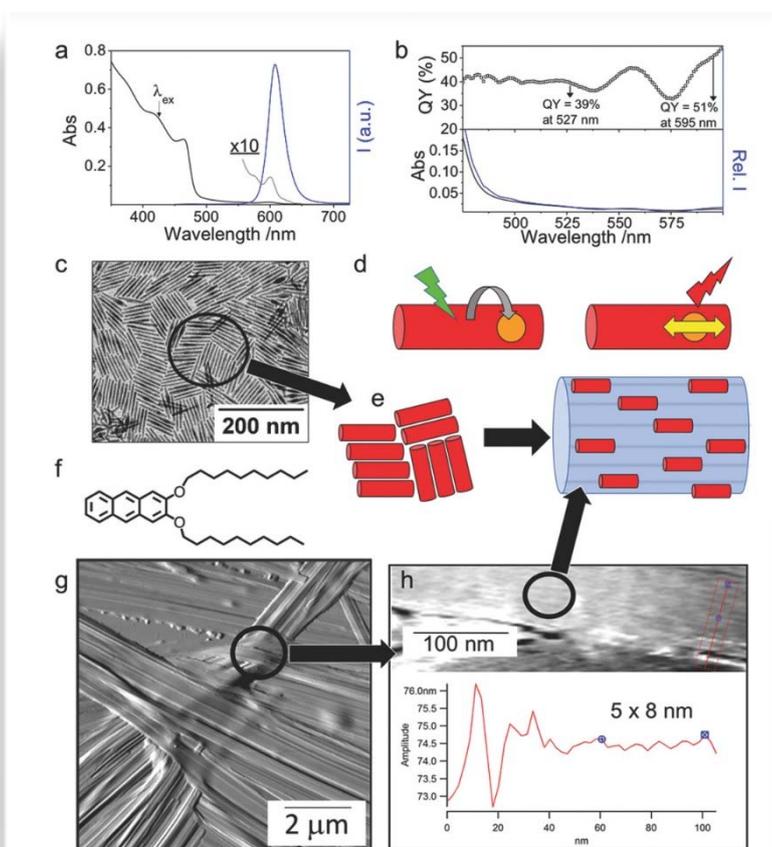


Figure. a) Absorption (black) and photoluminescence (PL, blue) spectra of 48 nm long CdSe-CdS QRs ($\lambda_{ex} = 425$ nm). CdSe core absorption peak is shown in gray and enhanced by a factor 10. b) (top panel) Variation of quantum yields of CdSe-CdS QRs with λ_{ex} ; (bottom panel) overlay of absorbance (black) and PL excitation spectra (blue) of 48 nm long CdSe-CdS QRs at $\lambda_{em} = 610$ nm. c) TEM images of CdSe-CdS QRs with $D = 6.2 \pm 0.7$ nm and $L = 64 \pm 3$ nm, $AR = L/D = 10$, showing 2D-smectic phases. d) Schematic representation of a sphere-in-rod QR: excitation occurs in the shell and energy transfer sensitizes the core, emission from the core is linearly polarized along the long axis of the QR. e) Representation of deaggregation of QRs (in red) by interaction with a DDOA nanofiber (NF in blue). f) Structure of the DDOA gelator. g) Atomic force microscopy (AFM) image of a dried DDOA (1×10^{-3} M)/QR (5×10^{-9} M) gel. h) High-resolution AFM amplitude image of a nanofiber from 1 g, revealing parallel packed fibrils (inset shows a profile corresponding to the red line demonstrating fibril widths of 8 nm).

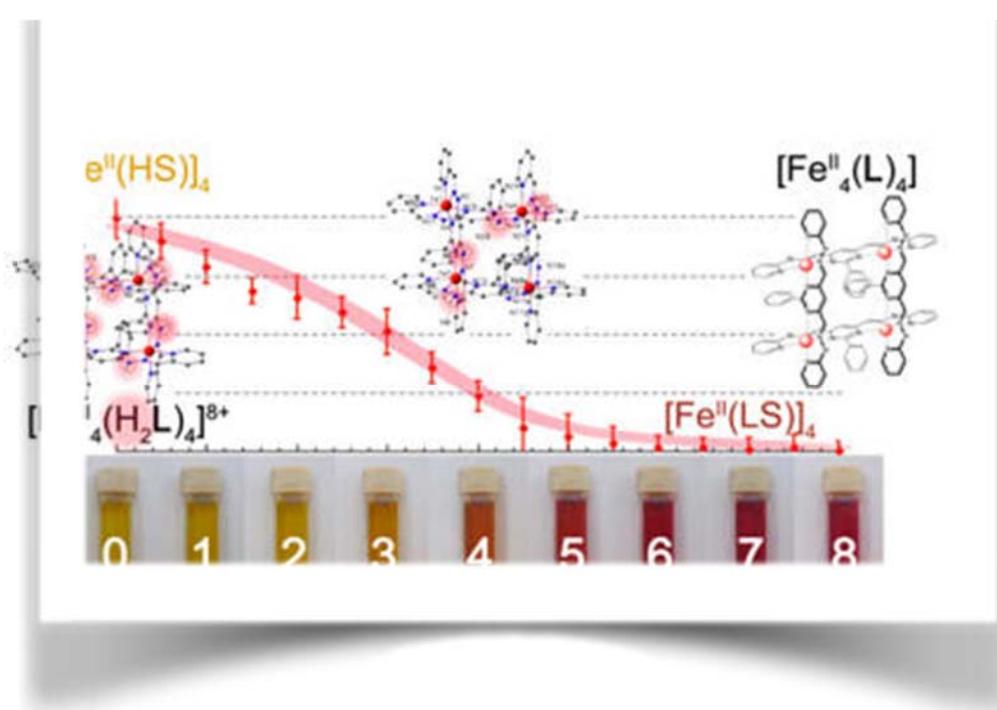
this work in which QRs and NFs interact, the orientation of each QR reveals information on the underlying nanostructure (such as surface striation, bundle formation, and helicity).

Dhers, S.; Mondal, A.; Aguila, D.; Ramirez, J.; Vela, S.; Dechambenoit, P.; Rouzieres, M.; Nitschke, J. R.; Clerac, R.; Lehn, J. M., Spin State Chemistry: Modulation of Ligand pK(a) by Spin State Switching in a 2x2 Iron(II) Grid-Type Complex. *Journal of the American Chemical Society* 2018, 140, 8218-8227, 10.1021/jacs.8b03735

CRPP, France/IISc Bangalore, India

The iron(II) [2X2] grid complex Fe-8H has been synthesized and characterized. It undergoes spin-crossover (SCO) upon deprotonation of the hydrazine-based terpyridine-like ligand. The deprotonation patterns have been determined by X-ray crystallography and H-1 NMR spectroscopy and discussed in relation to the spin state of the iron(II) centers, which influences greatly the pK(a) of the ligand. The synthesis of the magnetically silent zinc(II) analogue is also reported, and its (de)protonation behavior has been

characterized to serve as a reference for the study of the Fe-II grid complexes. DFT computations have also been performed in order to investigate how the successive deprotonation of the bridging ligands affects the SCO behavior within the grid.



Pal, A.; Prellier, W.; Murugavel, P., Spin-flop and magnetodielectric reversal in Yb substituted GdMnO₃. *Journal of Physics-Condensed Matter* 2018, 30, 125801. [10.1088/1361-648X/aaad3a](https://doi.org/10.1088/1361-648X/aaad3a)
IIT Madras India/CRISMAT, France

The evolution of various spin structures in Yb doped GdMnO₃ distorted orthorhombic perovskite system was investigated from their magnetic, dielectric and magnetodielectric characteristics. The Gd_{1-x}Yb_xMnO₃ ($0 \leq x \leq 0.15$) revealed an enhanced magnetodielectric coupling when their magnetic structure is guided from *ab* to the *bc*-cycloidal spin structure upon Yb doping. The compounds exhibit, magnetic field and temperature controlled spin-flop from *c* to *a*-axis. Additionally, magnetodielectric reversal is observed for the $x = 0.1$ sample which depends on both magnetic field and temperature. The resultant correlation between magnetic and electric orderings is discussed in the frame of symmetric and antisymmetric exchange interaction models. These findings provide further insight in understanding the magnetoelectric materials and importantly show a way to tune the magnetic and magnetodielectric properties towards better application potential.

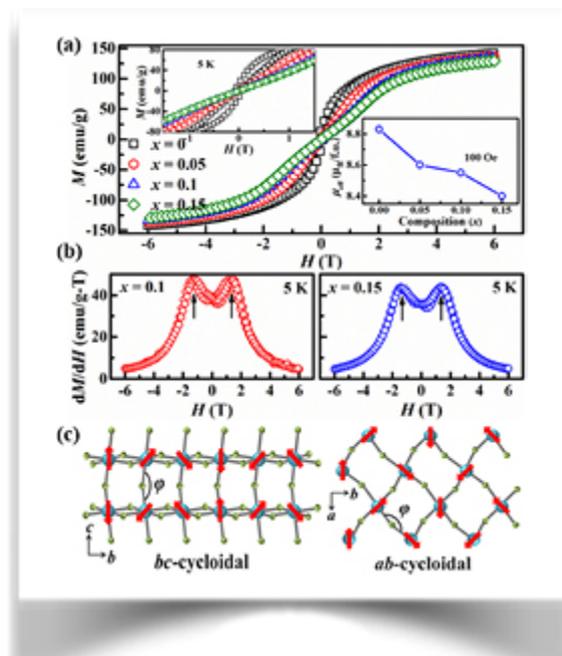


Figure. (a) M versus H plots for Gd_{1-x}Yb_xMnO₃ at 5 K from -6 T to 6 T. The upper inset shows the enlarged version of the plots near low fields and lower inset shows the μ_{eff} as a function of x . (b) dM/dH versus H plots at 5 K for $x = 0.1$ and 0.15 showing the H field induced spin-flop transition. (c) Schematics of *bc* and *ab*-cycloidal (CS) states where O²⁻ ion and Mn³⁺ spins are indicated as small spheres and large spheres with arrows.

EVENTS AND MEETINGS

A Workshop took place in Bangalore on October 17-19 2018



A call will be launched by the end of February for short term scientific mission exchanges for Students and young Researchers preferably. The rules are the following: The host lab pays for the accommodation of the visiting person who (or his/her lab) lab has to provide the funding for the travel

OTHER NEWS

2 Indian PhD students were hosted in the French laboratories for 3 months. While 12 visits by French Researchers were made by the LIA.

2 CEFIPRA Projects were deposited 2018.

New Magneto-Electric Hybrid Materials

Design, characterization and (photo)magnetism of hybrid molecular materials

The French part of the LIA and the CNRS would really appreciate that from now Researchers working in the framework of this LIA, go on acknowledging its support.

This is an example: We acknowledge financial support from the National Center for Scientific Research (CNRS) in the frame of the Indian-French Laboratory of Solid State Chemistry (LAFICS) program.