Dear Colleagues and friends,

I have been asked by the CNRS to be in charge of the French part of the Indian-French Laboratory of Solid State Chemistry. IFLaSC in English or LaFICS 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, Alsace public scientific and professional institutions and The Indian Institute of Science, Bangalore (IISC), an autonomous public institution funded by the government of India. Several laboratories and institutions linked to the CNRS, the UCBN and the IISC are involved in this LaFICS that are:

- the Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB)
- 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 Université de Strasbourg
- The Solid State and Structural Chemistry Unit, SSCU, 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 I wish to bring some more dynamism to this LIA and encourage Indians and French Researches 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.

I wish to associate Prof. Ramasesha, my co-Chair in India, to this initiative!

Enjoy your reading!

Marie Helene DELVILLE

Research highlights

Bag, P.; Chakraborty, A.; Rogez, G.; Chandrasekhar, V., Pentanuclear Heteronnetallic \{Mn(2)(III)Ln(3)\} (Ln = Gd, Dy, Tb, Ho) Assemblies in an Open-Book Type Structural Topology: Appearance of Slow Relaxation of Magnetization in the Dy(III) and Ho(III) Analogues. Inorganic Chemistry 2014, 53 (13), 6524-6533.

This article show that the reaction of Ln(III) nitrate and Mn(ClO4)2·6H2O salts in the presence of a multidentate sterically unencumbered ligand, (E)-2,2′-(2-hydroxy-3-(2-hydroxyphenylimino)methyl)-5-methylbenzylazanediyl)diethanol (LH4) leads to the isolation of four isostructural pentanuclear heterometallic complexes \[\text{[Mn}^{\text{III}}\text{2Ln}^{\text{III}}(\text{LH})_{4}(\text{NO}_3)(\text{HOCH}_3)]\text{ClO}_4\cdot\text{NO}_3\] (1), \[\text{[Mn}^{\text{III}}\text{2Dy}^{\text{III}}(\text{LH})_{4}(\text{NO}_3)(\text{HOCH}_3)]\text{ClO}_4\cdot\text{NO}_3\] (2), \[\text{[Mn}^{\text{III}}\text{2Tb}^{\text{III}}(\text{LH})_{4}(\text{NO}_3)(\text{HOCH}_3)]\text{ClO}_4\cdot\text{NO}_3\] (3), and \[\text{[Mn}^{\text{III}}\text{2Ho}^{\text{III}}(\text{LH})_{4}(\text{NO}_3)(\text{HOCH}_3)]\text{ClO}_4\cdot\text{NO}_3\] (4) with an open-book type structural topology. 1–4 are dicationic and crystallize in the achiral space group, \(P_{2_1}/n\). A total of four triply deprotonated ligands, \([\text{LH}]^{3-}\), are involved in holding the pentameric metal framework, \(\{\text{Mn}^{\text{III}}_{2}\text{Ln}^{\text{III}}\}\). In these complexes both the lanthanide and the manganese (III) ions are doubly bridged, involving phenolate or ethoxide oxygen atoms. The magnetochemical analysis reveals the presence of global antiferromagnetic interactions among the spin centers at low temperatures in all the four compounds. AC susceptibility measurements show the presence of temperature dependent out-of-phase \(ac\) signal for compounds 2 and 4 indicating an SMM behavior.
In this paper the authors show that a new ternary selenide Ba$_9$Fe$_4$Se$_{16}$ has been synthesized from the reaction of appropriate amounts of elements at high temperature in a silica sealed tube. The compound crystallizes in the tetragonal space group $I4_1/a$ with $a=10.0068(3)$ Å and $c=35.6415(9)$ Å, $Z=4$. It is an isostructural compound to the sulfide α-Ba$_9$Fe$_4$S$_{15}$, which is a high temperature polymorph of β-Ba$_9$Fe$_4$Se$_{15}$ that belongs to the indefinitely adaptive phases series Ba$_3$Fe$_{1+x}$S$_5$, $0 \leq x \leq 1$. X-ray powder diffraction and TEM analyses of the synthesized compound were used to determine the phase composition and the structure. The crystal structure can be viewed as overlapping sections along the $c$ axis. Those sections are formed by the coordination polyhedra around barium atoms which can be described as trigonal prisms and bidispensoids. Within the sections formed by barium polyhedra, isolated pairs of edge sharing FeSe$_4$ tetrahedra are found. Magnetic measurements performed on Ba$_9$Fe$_4$Se$_{16}$ indicate an antiferromagnetic behavior with Néel temperature of ~13 K. Possible influence of air exposure on the magnetic properties is also discussed here. The electric measurements show an insulating behavior below 160 K and the dielectric permittivity and loss tangent at the lowest frequency measured reveal a change of slope very close to $T_N$. However no magneto dielectric effect was evidenced for magnetic fields of up to 3 T. Activation energy, $E_A=0.18$ eV, was extracted from the AC conductivity plot in the temperature range of 160–300 K.


The authors here have studied the concentration-dependent near-Fermi-level valence-band electronic structure of Sm$_{0.1}$Ca$_{0.9-x}$Sr$_x$MnO$_3$ ($x=0$, 0.1, 0.3, and 0.6) using high-resolution ultraviolet photoelectron spectroscopy (HRUPS) across the metal insulator transition. At low temperatures (50 and 100 K), a transformation from pseudogap type behavior ($x=0$ and 0.1) to insulating behavior ($x=0.3$ and 0.6) is observed with an increase in Sr content. While at the high temperatures, the metallic like density of states appears
up to $x=0.3$ and then vanishes at $x=0.6$. The temperature-dependent spectra reveal a changeover from pseudogap to metallic like states for $x=0$ above its magnetic cluster-glass ordering temperature (110 K). In the case of $x=0.1$, the temperature-dependent change in the density of states is quite different from that of $x=0$ due to the weaker cluster-glass component and exhibits an interesting spectral weight transfer in the high-temperature paramagnetic phase. These findings would immensely help in understanding the puzzling charge transport scenario in Sm$_{1-Ca_{0.9-x}}$Sr$_x$MnO$_3$ from a microscopic point of view.


This paper deals with the development of a receptor with selectively functionalized at the lower rim of p-tert-butyl calix[4] arene linked through amide bond, resulting in the diamide derivatives (L-1, L-2 and L-3) suitable for sensing ions and molecules. All the derivatives were thoroughly characterized by analytical and spectral methods. These derivatives were structurally characterized by single crystal X-ray diffraction and the conformational features of the calix[4] arene as well as the pendants are discussed. The L-1 and L-2 exhibited intramolecular hydrogen bond interaction between the N-H and the lower rim phenolic oxygen in addition to the circular hydrogen bonding between the phenolic O-H and the ether oxygen of the adjacent strand. The corresponding H-bond is absent when no 'H' is present on amide-N as in case of L-3. Such intramolecular N-H dot O interactions observed with the pendant results in a conformational bend responsible for the orientation of the arms and there by the nature of the binding core formed. Thus the binding cores formed differ largely between L-3 and the other two.


Two oxazolidine nitroxide complexes of cobalt(II), 
$[\text{Co}^{II}(\text{L'}_2)](\text{B(C}_6\text{F}_5)_4)_2\cdot\text{CH}_2\text{Cl}_2$ (1) and $[\text{Co}^{II}(\text{L'}_2)](\text{B(C}_6\text{F}_5)_4)_2\cdot2\text{Et}_2\text{O}$ (2), where, L' is the tridentate chelator 4,4-dimethyl-2,2-bis(2-pyridyl)oxazolidine N-oxide, have been investigated by crystallographic, magnetic, reflectivity, and theoretical (DFT) methods. This work follows on from a related study on $[\text{Co}^{II}(\text{L}_2)](\text{NO}_3)_2$ (3), a multifunctional complex that simultaneously displays magnetic exchange, spin crossover, and single molecule magnetic features. Changing the anion and the nature of solvation in the present crystalline
species leads to significant differences, not only between 1 and 2 but also in comparison to 3. Structural data at 123 and 273 K, in combination with magnetic data, show that at lower temperatures 1 displays low-spin Co(II)-to-radical exchange with differences in fitted $J$ values in comparison to DFT (broken symmetry) calculated $J$ values ascribed to the sensitive influence of a tilt angle ($\theta$) formed between the Co(d$_z^2$) and the trans-oriented O atoms of the NO radical moieties in L. Spin crossover in 1 is evident at higher temperatures, probably influenced by the solvate molecules and crystal packing arrangement. Complex 2 remains in the high-spin Co(II) state between 2 and 350 K and undergoes antiferromagnetic exchange between Co–radical and radical–radical centers, but it is difficult to quantify. Calculations of the magnetic orbitals, eigenvalue plots, and the spin densities at the Co and radical sites in 1 and 2 have yielded satisfying details on the mechanism of metal–radical and radical–radical exchange, the radical spins being in $\pi^*_{NO}$ orbitals.


IPCMS, France/IITK, India/NISER, India

In this paper the reaction of hetero donor chelating mannich base ligand 6,6′-{(2-(dimethylamino)ethylazanediyl)bis(methylene)} bis (2-methoxy-4-methylphenol) with Ni(ClO$_4$)$_2$·6H$_2$O and lanthanide(III) salts [Dy(III) (1); Tb(III) (2); Gd (III) (3); Ho(III) (4); and Er(III) (5)] in the presence of triethylamine and pivalic acid afforded a series of heterometallic hexanuclear Ni(II)–Ln(III) coordination compounds, [Ni$_3$Ln$_3$(μ$_3$-O)(μ$_3$-OH)$_3$(L)$_3$(μ-OOCMe$_2$)$_3$](ClO$_4$)$_w$CH$_3$CN·xCH$_2$Cl$_2$·yCH$_3$OH·zH$_2$O [for 1, $w = 8$, $x = 3$, $y = 0$, $z = 5.5$; for 2, $w = 0$, $x = 5$, $y = 0$, $z = 6.5$; for 3, $w = 15$, $x = 18$, $y = 3$, $z = 7.5$; for 4, $w = 15$, $x = 20$, $y = 6$, $z = 9.5$; and for 5, $w = 0$, $x = 3$, $y = 2$, $z = 3$]. The molecular structure of these complexes reveals the presence of a monocationic hexanuclear derivative containing one perchlorate counteranion. The asymmetric unit of each of the hexanuclear derivatives comprises the dinuclear motif [NiLn(L)(μ$_3$-O)(μ$_3$-OH)(μ-Piv)]. The cation contains three interlinked O-capped clusters: one Ln$_3$O and three Ni$_2$Ln$_2$O. Each of the lanthanide centers is eight-coordinated (distorted trigonal-dodecahedron), while the nickel centers are hexacoordinate (distorted octahedral). The study of the magnetic properties of all compounds are reported and suggests single molecule magnet behavior for the Dy(III) derivative (1).
In this paper the authors reported Insertion of lithium into the jarosite hydroxysulfate $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$ leads to an amorphous phase $\text{Li}_{2+x}\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$ (with $0 < x < 0.5$), through a biphasic mechanism. The latter phase exhibits reversible electrochemical lithium intercalation/deintercalation through a solid-solution-like process, leading back to the oxidized jarosite $\text{Li}_x\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$ (with $0.3 < x < 0.6$), with redox cycling at 2.82 V and a capacity of 110 mAh/g at C/20. This unique topotactic reaction between an amorphous and a well-crystallized phase is interpreted on the basis of the formation of an inorganic polymer.

In this paper, the local epitaxial growth of pulsed laser deposited Ca$_2$MnO$_4$ films on polycrystalline spark plasma sintered Sr$_2$TiO$_4$ substrates was investigated to determine phase formation and preferred epitaxial orientation relationships (ORs) for isostructural Ruddlesden-Popper (RP) heteroepitaxy, further developing the high-throughput synthetic approach called Combinatorial Substrate Epitaxy (CSE). Both grazing incidence X-ray diffraction and electron backscatter diffraction patterns of the film and substrate were indexable as single-phase RP-structured compounds. The optimal growth temperature (between 650 °C and 800 °C) was found to be 750 °C using the maximum value of the average image
quality of the backscattered diffraction patterns. Films grew in a grain-over-grain pattern such that each Ca2MnO4 grain had a single OR with the Sr2TiO4 grain on which it grew. Three primary ORs described 47 out of 49 grain pairs that covered nearly all of RP orientation space. The first OR, found for 20 of the 49, was the expected RP unit-cell over RP unit-cell OR, expressed as [100][001] film ||[100][001] sub. The other two ORs were essentially rotated from the first by 90°, with one (observed for 17 of 49 pairs) being rotated about the [100] and the other (observed for 10 of 49 pairs) being rotated about the [110] (and not exactly by 90°). These results indicate that only a small number of ORs are needed to describe isostructural RP heteroepitaxy and further demonstrate the potential of CSE in the design and growth of a wide range of complex functional oxides.


Oxides containing magnetic 3d transition metals offer a large family of structures with frustrated magnetic networks. Some of these incommensurate antiferromagnetic structures are responsible for the local breaking of inversion symmetry so that these oxides are called spin-induced ferroelectrics. As listed in the introduction of this short review, the number of these multiferroics continues to increase. As for applications, the coupling between these ferroisms is needed; some magnetic oxides, despite a lack of ferroelectric ground state, exhibit large magnetoelectric coupling with a magnetic-field-induced polarization. Thus, they are classified as “magnetoelectrics”. In the present review, they focus on recently studied systems showing ferroelectric-like behaviors or large magnetoelectric coefficients. This will be illustrated by chromites with the comparison between ceramics of CuCrO2 and AgCrS2: they exhibit different antiferromagnetic ground states, centrosymmetric and noncentrosymmetric. For the magnetoelectrics, the example of the cobaltite, CaBaCo4O7, which is a polar ferrimagnet, is taken to illustrate the existence of large magnetoelectric coefficients in crystals. Then, the existence of spin-induced ferroelectricity in centrosymmetric orthochromites (RECrO3 with RE = Lu or Er) is discussed. Through this selection of potential multiferroics or magnetoelectrics, it is clear that many magnetic materials in different forms (bulk/crystal/thin film) remain to be studied.

CRISMAT, France/ Venkatesh Gopal who did his Msc in Coimbatore Institute of Technology, Coimbatore, Tamil Nadu, India, and joined the CRISMAT under the recommendation of Prof. V.V. Raju (IIT Madras).

A brief description of research advances in the area of short-pulse-laser nanostructuring of thin Au films is made followed by examples of experimental data and a discussion of the results on the characterization of structural and optical properties of gold nanostructures. These consist of partially spherical or spheroidal nanoparticles (NPs) which have a size distribution (80 ± 42 nm) and self-organization characterized by a short-distance order (length scale ≈140 nm). For the NP shapes produced, an observably broader tuning range (of about 150 nm) of the surface plasmon resonance (SPR) band is obtained by renewal thin film deposition and laser annealing of the NP array. Despite the broadened SPR bands, which indicate damping confirmed by short dephasing times not exceeding 4 fs, the self-organized Au NP structures reveal quite a strong enhancement of the optical signal. This was consistent with the near-field modeling and micro-Raman measurements as well as a test of the electrochemical sensing capability.

Pravarthana, D.; Trassin, M.; Chu, J. H.; Lacotte, M.; David, A.; Ramesh, R.; Salvador, P. A.; Prellier, W., BiFeO3/La0.7Sr0.3MnO3 heterostructures deposited on spark plasma sintered LaAlO3 substrates. *Applied Physics Letters* 2014, 104 (8), 082914 (1-6).

CRISMAT, France/ D. Pravarthana who did a MSs. IISER at PUNE before joining CRISMAT for his PhD done under the supervision of Dr. W. Prellier.

Multiferroic BiFeO3 (BFO)/ La0.7Sr0.3MnO3 heterostructured thin films were grown by pulsed laser deposition on polished spark plasma sintered LaAlO3 (LAO) polycrystalline substrates. Both polycrystalline LAO substrates and BFO films were locally characterized using electron backscattering diffraction, which confirmed the high-quality local epitaxial growth on each substrate grain. Piezoforce microscopy was used to image and switch the piezo-domains, and the results are consistent with the relative orientation of the ferroelectric variants with the surface normal. This high-throughput synthesis process opens the routes
towards wide survey of electronic properties as a function of crystalline orientation in complex oxide thin film synthesis.


Department of Chemistry Visva-Bharati University, India/ CRISMAT, France

In this report Raveau and coworker reviewed the control of the spin orientation transitions in perovskites containing manganese, cobalt, iron, and chromium, based on crystal chemistry factors. They describe herein the effect of the size and of the magnetic nature of the $\text{Ln}^{3+}$ cations and of the doping and large substitutions at the octahedral sites. Spin blockade introduced by nanostructural effects and magnetic anisotropy induced by laser pulse application are also discussed.

**Ravindra, A. V.; Behera, B. C.; Padhan, P.; Lebedev, O. I.; Prellier, W., Tailoring of crystal phase and Neel temperature of cobalt monoxides nanocrystals with synthetic approach conditions. Journal of Applied Physics 2014, 116 (3).**

IITM Madras, India/ CRISMAT, France

Cobalt monoxide (CoO) nanocrystals were synthesized by thermal decomposition of cobalt oleate precursor in a high boiling point organic solvent 1-octadecene. The X-ray diffraction pattern and transmission electron microscopy studies suggest that pure face-centered-cubic (fcc) phase of CoO can be synthesized in the temperature range of 569–575 K. Thermolysis product at higher synthesis temperature 585 K is a mixture of fcc and hexagonal-closed-packed (hcp) phases. These nanocrystals are single crystals of CoO and exhibit mixture of two types of morphologies; one is nearly spherical with 5–25 nm diameter, and other one is 5–10 nm thick flake. The pure fcc-CoO nanocrystals show enhanced, and mixture of fcc- and hcp-CoO nanocrystals show reduced antiferromagnetic ordering temperature. Such results provide new opportunities for optimizing and enhancing the properties and performance of cobalt oxide nanomaterials.

**Saradhi, M. P.; Lakshminarasimhan, N.; Boudin, S.; Gupta, K. V. K.; Varadaraju, U. V.; Rayeau, B., Enhanced luminescence of Sr$_2$SiO$_4$:Dy$^{3+}$ by sensitization (Ce$^{3+}$/Eu$^{2+}$) and fabrication of white light-emitting-diodes. Materials Letters 2014, 117, 302-304.**

IITM Madras, India/ CRISMAT, France

The role of sensitization by co-doping Ce$^{3+}$/Eu$^{2+}$ in the Sr$_2$SiO$_4$:Dy$^{3+}$ phosphor system is studied with a view of improving the emission properties and chromaticity coordinates. The concentration
dependence of the emission intensity of Dy$^{3+}$ in Sr$_2$–xDy$_x$Li$_x$SiO$_4$: ($x=0.01$–$0.05$ in steps of $0.01$) is studied, and the critical concentration is found to be 3 mol% Dy$^{3+}$ per formula unit. Partial energy transfer from Ce$^{3+}$ to Dy$^{3+}$ is observed, and the luminescence intensity of Dy$^{3+}$ is enhanced. It is also found that Eu$^{2+}$, Ce$^{3+}$ containing compositions show better white emission than the corresponding Sr$_2$SiO$_4$:Dy$^{3+}$. LEDs fabricated by coating the ultraviolet (UV) emitting chips with the synthesized phosphor compositions show bright white emission with reasonable chromaticity coordinates.

Sasmal, A.; Bauza, A.; Frontera, A.; Rizzoli, C.; Desplanches, C.; Charbonniere, L. J.; Mitra, S., Relevant and unprecedented C-H/sigma supramolecular interactions involving sigma-aromatic M2X2 cores. 


Department of Chemistry, Jadavpur University, India/ICMCB, France

A novel type of C–H/σ supramolecular interaction involving σ-aromatic M$_2$X$_2$ ($M = Cu$, Hg; $X = Cl$, Br, I, S) cores is reported for the first time. Three new polymeric coordination copper complexes, {[Cu(μ-Cl)(μ-L)]$_2$}$_n$ (1), {[Cu(μ-I)(μ-L)]$_2$}$_n$ (2) and [Cu(Br)$_2$(μ-L)(CH$_3$CN)$_2$]$_2$ (3), have been synthesized with the organic ligand α,ω-bis(benzotriazoloxy)propane system (L) and halides as counterions. A very interesting C–H/σ supramolecular interaction has been observed in the solid state structure of compound 2, similar to a C–H⋯π interaction, which has been confirmed by Bader’s “atoms-in-molecules” AIM analysis. The Nucleus Independent Chemical Shift (NICs) method was used to evaluate the aromatic character of the different cores in this study. The influence of the nature of the metal ions, bridging atoms, oxidation states, and coordination environments around the metal centers on the strength of the aromaticity of the M$_2$X$_2$ cores was theoretically analyzed and explained. The binding ability of the 1-alkoxy-1,2,3-benzotriazole ring to establish π–π and C–H/π interactions and how its coordination to Cu(I) and Cu(II) ions affects the strength of the aforementioned interactions have been discussed. The electron deficient triazole ring and its π-acidity increases upon coordination of the Cu ion, leading to the formation of a lone pair (lp)–π interaction involving the five-membered ring of the ligand, which has also been analyzed. They have also analyzed the C–H/σ interactions of previously reported X-ray crystal structures of different coordination polymers based on a binuclear copper(I) complex and 2,3-dimethylpyrazine, dithioethers, and benzotriazol-1-yl-based pyridyl units as ligands using I$^-$ as a counter-ion. Complex 1 shows antiferromagnetic behavior with a magnetic coupling constant of $J = -7.9$ cm$^{-1}$. Moreover, photoluminescence and TGA studies of the complexes were also carried out.

Department of Chemistry, Jadavpur University, India/ICMCB, France

The reversible redox isomerisms in first row transition metal complexes of the type ML₂ were studied. The six ML₂ complexes (M = MnIII (1), FeII (2), CoIII (3), NiII (4), CuII (5) and ZnII (6)) were synthesized with a redox active Schiff base ligand [2-(3,5-di-tert-butyl-2-hydroxyphenyl amino)-4-chlorophenol] (H₃L) presenting different oxidation states from −2 to 0 (L²⁻, L⁻ and L⁰). EPR spectra and magnetic susceptibility measurements indicate the presence of complexes of the type [MnIII(L²⁻)(L⁻)] (1) with S = 1/2, [FeII(L⁻)₂] (2) with S = 2, [CoIII(L²⁻)(L⁻)] (3) with S = 1/2, [NiII(L⁻)₃] (4) with S = 1, [CuII(L⁻)₂] (5) with S = 1/2 and [ZnII(L⁻)₂] (6) with S = 0 at high temperatures. Temperature and solvents influence the electronic structures of the species and give several valence tautomers. At low temperatures these complexes present thermally induced metal-to-ligand (1, 2, 4) or ligand-to-ligand (in 5, 6) electron transfer (partial or total), resulting in compounds of the type [MnIV(L²⁻)] (1') with S = 1/2, [FeIII(L⁻)(L²⁻)] (2') with S = 1, [NiIII(L²⁻)(L⁻)] (4') with S = 0, [CuII(L²⁻)(L⁰)] (5') with S = 1/2 and [ZnII(L⁻)] (6') with S = 1. This electron transfer is in agreement with the general trend in the redox potentials of the first row transition metal ions from Mn(II) to Zn(II), and it allows them to prepare and stabilize reversibly switchable tautomeric forms in transition metal complexes with redox-active ligands.


Department of Chemistry Visva-Bharati University, India/CRISMAT, France

The effect of oxygen/cobalt off-stoichiometry upon magnetism in CaBaCo₄O₇ has been investigated. It is shown that the oxides CaBaCo₄O₇+δ and CaBaCo₄-xO₇-δ (0 ≤ x ≤ 0.20) synthesized below 1100 °C in air exhibit phase separation, where ferrimagnetic regions with Tc~56 K to 64 K coexist with regions of magnetic clusters. The latter are detected from ac-susceptibility measurements, which show various frequency dependent peaks at ~14–20 K, 37 K, and 45 K, depending on the stoichiometry. The origin of this phenomenon is attributed to the great sensitivity of the material to oxidation as the synthesis of temperature is lowered, leading to the introduction of additional Co³⁺ cations, with respect to the ideal formula CaBaCo₂⁺⁺Co³⁺O₇. This excess Co³⁺ tends to destroy the ferromagnetic zig-zag chains of the ferrimagnetic structure and...
creates various cobalt spin clusters, leading to the inherent phase separation in the samples.

Seikh, M. M.; Caignaert, V.; Lebedev, O. I.; Raveau, B., Cubic structure and canted antiferromagnetism of CaMn7O12 doped with trivalent cations (Fe, Al, Cr). Solid State Communications 2014, 180, 52-55. Department of Chemistry Visva-Bharati University, India/ CRISMAT, France

In this study, the authors show the dramatic effect of the doping of the octahedral sites with M3+ cations (Fe3+, Al3+ and Cr3+) upon the structure and magnetism of the rhombohedral double perovskite CaMn3O12. In the oxides CaMn_{7-x}M_xO_{12}, charge ordering between Mn3+ and Mn4+ octahedral sites is destroyed leading to the cubic structure (Im-3), whereas the initial magnetic properties (TN~90 K) have disappeared leading to canted antiferromagnetism (TN~50–70 K) for small x values (x~0.2–1). A spin glass like behaviour is also observed for larger values (x~1) in the case of Fe substitution.


The authors report on the impact of zinc doping upon the magneto-electric properties of CaBaCo4O7. They show that the presence of less than 1% Zn at the Co sites decreases TC from 64 K to 48 K and generates two magnetic transitions, concomitant with changes of slope of dielectric permittivity, at 54 K and 77 K, respectively. Powder neutron diffraction and magnetic data show the existence of an incommensurate magnetic phase and a spin-flop transition in this temperature range. The crossover of the magnetodielectric effect of this oxide, from positive below 50 K to negative above this temperature emphasizes the primordial role of the incommensurate magnetic phase in the evolution of these properties.
Seikh, M. M.; Caignaert, V.; Sundaresan, A.; De, C.; Raveau, B., Ti-rich double perovskites LnCu$_3$$-y$Ti$_2$$-x$Mn$_{2+x+y}$O$_{12}$: ferrimagnetism and magnetoresistance up to room temperature. Journal of Materials Chemistry C 2014, 2 (30), 6061-6067.
Department of Chemistry Visva-Bharati University, India/ CRISMAT, France

Ti-rich double perovskites LnCu$_3$$-y$Ti$_2$$-x$Mn$_{2+x+y}$O$_{12}$ have been synthesized at normal pressure, with a wide homogeneity range, $0 < x < 0.5$ and $0 < y \leq 1$. All these oxides are ferrimagnetic, with $T_C$ ranging from 160 K to 293 K, in spite of the high 3d$^0$-Ti content in the octahedral sites. The evolution of $T_C$ can be monitored on the basis of three factors-antiferromagnetic superexchange interactions Cu$^{2+}$$\uparrow$–O–Mn$^{3+}/4+$$\downarrow$–O–Cu$^{2+}$$\uparrow$, double exchange Mn$^{4+}$–O–Mn$^{3+}$ interactions in the octahedral sites and chemical pressure due to the size effect of Ln$^{3+}$. Differently from high pressure synthesized manganites, these oxides exhibit maximum magnetoresistance at $T_C$, similar to single perovskite manganites. Intrinsic magnetoresistance can thus be obtained at room temperature, but with a smaller amplitude compared to single manganites, due to the dilution effect of titanium.

Department of Chemistry Visva-Bharati University, India/ CRISMAT, France

The isovalent substitution of strontium for barium in CaBaCo$_4$O$_7$ destroys the ferrimagnetism in a striking way though it keeps the same orthorhombic crystal symmetry and cobalt valence as the parent phase. The gradual weakening of ferrimagnetism in CaBa$_{1-x}$Sr$_x$Co$_4$O$_7$ ($0 < x \leq 0.10$) leaves place to magnetic frustration together with antiferrimagnetism. The phase separation that appears, due to the strong competition between long range ferrimagnetic ordering and magnetic frustration, is interpreted by local melting of charge ordering. The latter originates from local structural distortion around the Ba(Sr) site. The dynamic scaling theory, $\tau = \tau_0(T_f/T_g - 1)^{-z\nu}$, suggests that the frustrated magnetic phase is cluster glass in nature with strongly interacting spins. This finding reveals that the orthorhombic symmetry in CaBaCo$_4$O$_7$ is not a sufficient condition to manifest ferrimagnetic ordering.
Sodium insertion into the vanadate NaVO₃ shows the formation of an amorphous phase with the composition Na₁₋₃₋₇yVO₃. The latter phase exhibits reversible electrochemical sodium intercalation/deintercalation properties through a solid solution-like process, for 0 < y < 0.7, with redox cycling at 1.8 V vs. Na⁺/Na and a capacity of 150 mAh/g. This result opens the route to the investigation of amorphous matrices involving transition metal oxides for sodium ion battery applications.

Department of Chemistry Visva-Bharati University, India/ CRISMAT, France
As part of our common activities, Please find attached the numbers of collaborative papers since 2009 and in 2014 for both sides!