GARNET-TYPE NANOCRYSTALS FOR *IN VIVO* BIO-IMAGING AND NANOTHERMOMETRY

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Summary: Neodymium-doped garnets have been widely developed during roughly the last sixty years and have been an outstanding fluorescent material. It has been considered as the gold standard among multipurpose solid state lasers. Yet, the successful downsizing of this system into the nano regimen has been elusive, so far. Indeed, the synthesis of a garnet structure at the nanoscale, with enough crystalline quality for optical applications was found to be quite challenging.

First, I will present an improved solvothermal synthesis method producing Nd^{3+}-doped $Y_3Al_5O_{12}$ (YAG:Nd^{3+}) and $Gd_3Sc_2Al_3O_{12}$ (GSAG:Nd^{3+}) nanocrystals of remarkably good structural quality and controlled size in the range 50 to 200 nm.[1] These features allow for high photoluminescence efficiency, leading to the development of thermosensitive near-infrared (NIR) light-emitting nanoparticles. Second, I will show how to stabilize these YAG:Nd^{3+} and GSAG:Nd^{3+} nanocrystals in aqueous solutions, a key requirement for use in biomedical applications. Stabilization was successful achieved thanks to the use of asymmetric double-hydrophilic block copolymers, constituted of a metal-binding block and a neutral water-soluble block.[2] These newly stabilized YAG:Nd^{3+} nanoprobes offer long lifetimes and, more importantly, narrow emission lines that have been exploited by differential NIR fluorescence imaging, thus achieving an autofluorescence-free *in vivo* readout at the deep tissue level.[2] Finally, nanothermometry measurements, based on the ratiometric fluorescence of the YAG:Nd^{3+} and GSAG:Nd^{3+} nanocrystals, will be presented. GSAG:Nd^{3+} nanocrystals exhibit a maximal relative thermal sensitivity of 0.20 % $°C^{-1}$, higher than that of YAG:Nd^{3+} nanocrystals due to the difference in the crystal field of the host matrices.[3] These results pave the way for the use of these garnet-type nanocrystals as multifunctional nanoplatforms for *in vivo* biophotonics.

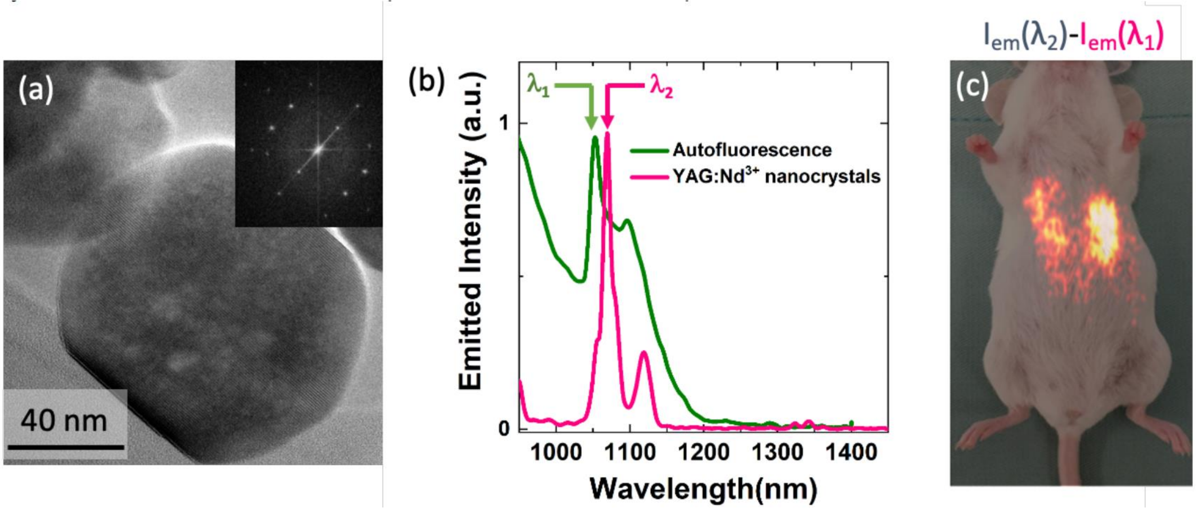

Fig. 1 (a) TEM image of a well-crystallized YAG:Nd^{3+} nanocrystal. (b) Fluorescence spectra of a colloidal solution of stabilized YAG:Nd^{3+} nanocrystals in PBS and of the whole body of a mouse (exc. 808 nm). (c) Differential hyperspectral fluorescence *in vivo* imaging with stabilized YAG:Nd^{3+} nanocrystals.

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SYNTHESES IN POLYOL MEDIUM OF INORGANIC OXIDES WITH VARIOUS SMART OPTICAL PROPERTIES

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Keywords: inorganic oxides, optical materials, electrochromic, photochromic, thermochromic properties

Summary: At the interface of the studies performed by 4 ICMCB's PhD students: Shian Guan (2017-2020),[1] Marie Bourdin (2016-2019),[2] Ines Andron (2017-2020),[3] Isabelle Trenque (2012-2015),[4] a single synthesis route: polyol mediated synthesis, was used with success for different inorganic oxides; the application field being smart optical compounds in both cases. This synthesis route has allowed us to develop nanoparticles of zinc oxide, vanadium oxide or tungsten oxide. This route is with easy implementation, inexpensive and with large scale production potentialities and leads to materials of high purity. Additionally, polyol route allows the obtaining of nano-crystalline oxides with uniform particle size distribution, tunable oxygen sub-stoichiometry thanks to the reducing properties of the polyol solvents. Then, the as-prepared NPs can be used in suspensions to be coated for the elaboration of transparent thin films from dip or spin-coating processes. The obtaining by this route of nanometric particles, however perfectly crystalline, has notably led to the possibility of doping these matrix materials with high doping ion concentrations (high solubility limits).

Thus, as first example, Al^{3+} or Ga^{3+} doped-ZnO powder, with high doping rate in comparison with the literature, exhibits remarkable infrared absorption properties thanks to their high free carrier density. Note also that due to the narrow particle size distribution of the as-prepared nanometric doped-ZnO powder, original correlation between crystallite size and unit-cell parameters have been established.

Also, in a second example, depending on the annealing atmosphere use to treat vanadium precursors, VO_2, V_2O_3 or V_2O_5 oxides with thermochromic or electrochromic properties can be obtained without any impurity, despite the versatility of the oxidation state of vanadium. This is of more particularly interest on vanadium dioxide, a relatively difficult-to-prepare oxide, whose first-order metal-insulator phase transition is widely explored in the literature for its thermochromic behavior (in smart windows with optimal thermal insulation).

Finally, polyol synthesis routes were performed to prepare some nanoparticles (NPs) of WO_{3-x}, MoO_{3-x} and $Zn_{1+\varepsilon}O$ oxides. The photochromic properties of WO_{3-x} as powder or thin films show improved optical contrasts between colored and bleached state with a self-bleaching behavior allowing their use them as smart films for solar control on glass windows. The mixing of molybdenum and zinc oxides, thanks to the creation of Schottky barriers at the solid / solid interface, lead to exceptional photochromic effect thanks to the possibility to activate under UV-light excitation of a self-closed redox reaction at this interface. Details on their optical spectra, the kinetic aspects through coloring or bleaching half-cycle and the cycling possibilities of the enhanced photochromic effects on WO_{3-x} oxides and ZnO/MoO_3 mixtures will be presented. Correlations between the optical properties of these nanoparticles and their micro-structural behavior (surface chemical composition vs bulk chemical composition) structural modifications, electronic transport: "polaronic" vs "plasmonic" effects, etc…) will be emphasized.

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METAL OXYSULFIDE NANOPLATES: GROWTH MECHANISM AND REACTIVITY, FROM LANTHANIDES TO TRANSITION METALS

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Keywords: oxysulfides; lanthanide; molybdenum; x-ray absorption spectroscopy; nucleation and growth

Summary: Metal Oxysulfides ($M_xO_yS_z$), in which the sulfur atoms are reduced (eg. S^{-II}), lie at the cross-roads of oxides (M_xO_y) and sulfides (M_xS_y): they present unique properties and still represent a synthetic challenge. The quest for efficient nanophosphors, with applications in lightening technologies and nanomedicine, raised the interest for oxysulfide nanoparticles in the 2000's. While bulk oxysulfides are usually prepared from the sulfidation of oxides at high temperature, Ln_2O_2S nanocrystals (Ln = lanthanide, Fig. 1) are formed in organic media below 350 °C.[1,2]

We produced metal oxysulfide nanoparticles by colloidal synthesis. We obtained unprecedented Ce_2O_2S nanoparticles as well as $(Gd,Ce)_2O_2S$ nanoparticles with Gd:Ce ratio from 0 to 100 %, forming a solid solution. The interest of cerium lies in its unique electronic properties in the lanthanide series. Ce_2O_2S is indeed the only lanthanide oxysulfide with a low bandgap (Eg < 2 eV), while the others are wide-gap semiconductors (Eg > 3 eV). Moreover, we evidenced that the 2-nm thick nanoplates showed a direct bandgap, instead of the expected indirect bandgap.[3]

Using Near-ambient-pressure XPS and XANES at S K-edge, we demonstrated that the nanoparticles were stable in air up to 40 % of cerium.[4] We then investigated the local structure of the nanoparticles, in relation with the presence of sodium in the reaction medium. At the time, sodium was considered a dopant in the structure.[2] Thermogravimetric analysis coupled to mass spectrometry was used to identify the surface ligands on the nanoparticles,[5] while SAXS-WAXS measurements evidenced the formation of a lamellar mesophase during the synthesis.[6] We confirmed by pair-distribution function analysis that Na was not a dopant in the nanoparticles. Lastly, we investigated the possibility to dope the nanoplates with molybdenum ions and form mixed compounds.

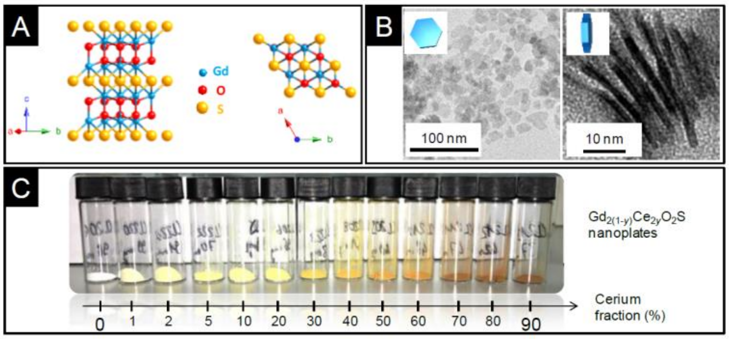

Fig. 1 (A) Gd_2O_2S structure. (B) Hexagonal nanoplates of $Gd_{1.25}Ce_{0.75}O_2S$. (C) Evolution of the powder colors along the series of $(Gd,Ce)_2O_2S$ nanoparticles.

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LOCALIZED *VS.* ITINERANT ELECTRONS IN GaV_4O_8

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Summary: Mixed-valent transition-metal compounds display complex structural, electronic and magnetic properties, which often intricately coexist. Here, we report the new ternary oxide GaV_4O_8, a structural sibling of skyrmion-hosting lacunar spinels.

GaV_4O_8 crystallizes in a hexagonal structure, S.G. *P*63*mc,* with a = 5.667(1) Å and c = 9.356(1) Å cell parameters. Although the cooperative polar arrangement of GaO_4 Tetrahedra (*Td*) remains, it differs from the lacunar spinel in the X stacking sequence (ABC) being ABAC for the oxide.

GaV_4O_8 reveals the smallest vanadium trimer known to date (2.52 Å vs 3.14 Å for V-V distances) and an original spin-orbital-charge texture that forms upon the structural phase transition at T_S = 68 K followed by the magnetic transition at T_N = 35 K. The texture arises from the simultaneous presence of orbital molecules on the vanadium trimers and localized electrons on the remaining vanadium atoms. Such hybrid electrons create new opportunities for novel types of spin, charge, and orbital order in mixed-valent transition metal compounds.

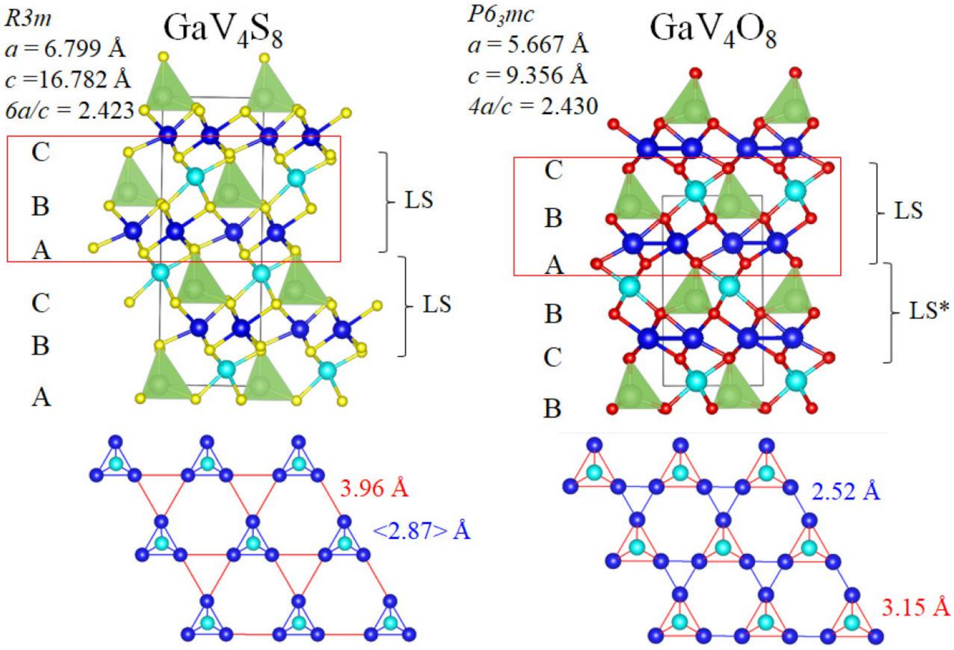

Fig. 1 Comparison between GaV_4S_8 and GaV_4O_8 structures.

LI-ION BATTERIES MATERIALS: THE POWER OF POWDER DIFFRACTION

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Keywords: battery materials; crystal structure, powder diffraction

Summary:

For improving lithium ion batteries, finding new electrode materials, determining their structure and being able to follow their structural evolution on charge and discharge is essential and powder diffraction is a method of choice. In this talk, I will present the strategy we use at the lab “Chimie du Solide et Energie” at Collège de France (Paris) to get useful information from diffraction experiments on battery materials, and how important a rigorous analysis of these data is for a reliable characterization. The talk will be illustrated by examples based on neutron and X-ray powder diffraction both in the field of electrode materials and ionic conductors, the developments of the latter being an important step towards the development of safe all-solid-state batteries.