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Georges Boulon
Emeritus Professor

Research programs: highlights since 1965

at the Physical Chemistry of Luminescent Materials Laboratory (LPCML) and then at the Institute Light Materials (iLM) of UCBLyon1, associated to CNRS.
http://pcml.univ-lyon1.fr/ http://ilm.univ-lyon1.fr/luminescence
Directors of LPCML:
1960-1982: Dr. Françoise GAUME, DR CNRS
1983-1994: Pr. Georges BOULON, Pr UCBLyon1
1995-2006: Dr. Christian PEDRINI, DR CNRS
2007- 2012: Dr. Marie-France JOUBERT, DR CNRS
Directors of iLM:
2013-2016:Dr. Marie-France JOUBERT, DR CNRS
2017-2020:Dr Philippe DUGOURD, DR CNRS
2021- :Dr Philippe DUGOURD, DR CNRS

I started research activities at the end of 1965 on Photoluminescence Processes and Excited State Dynamics of Bi^{3+} ions in (Ca,Sr) antimonates, (Y,Sc,Gd) sesquioxides and (Y,Sc,Gd) Orthovanadates, and was awarded "Docteur ès Sciences" (Third Cycle on Spectronomy) on March 1st, 1968 under the guidance of **Dr. Françoise GAUME, CNRS Director of Research, and Joseph JANIN Prof. University of Lyon,** then "Docteur d'Etat ès Sciences Physiques" on June 1st, 1970 under the guidance of **Dr. Françoise GAUME, CNRS Director of Research, and Prof. Daniel CURIE, Professor at the University of Paris**.

Then, after 1970, as so-called "Maître-Assistant of the University of Lyon", **Dr. Françoise GAUME** asked me, to help her for assisting new PhD students joining her at the LPCML group. From 1968 I have trained few PhD students up to my nomination of Professor of the UCBLyon1 (1981). I am very pride by this period of my scientific life, for which in addition of my regular lectures with undergraduate students, I spent my research time in co-operation with **Dr. Françoise GAUME** to train new PhD researchers as **C.PEDRINI, B. JACQUIER, R. MONCORGE, B.MOINE, M.F. JOUBERT,** who were all nominated **CNRS Researchers** later on**.** I have obviously to mention during these years the first mutual works of **my long co-operation with prof. R.Reisfeld from the Hebrew University of Jerusalem (Israel**) and two invitations in the USA which were also very important for my future scientific activities, **as Associated Researcher at the Wisconsin University,** Department of Physics with Professor W.Yen. (6 months on July-December 1978) and as **Invited Professor at the Oklahoma State University,** Department of Physics with Professor Powell (3 months on June-September 1982).

After my nomination of Full Professor in 1981, **Dr. Françoise GAUME** recommended me in 1983 to CNRS to be her successor at the head of the LPCML laboratory after her retirement. I was confirmed by this proposition by the UCBLyon1 and also accepted by the LPCML Committee in Lyon. I was very pride to be **Dr. Françoise GAUME's** successor. In France, CNRS laboratory directors are nominated for only 4 years, but it is also possible to continue two or even three times, depending of the acceptance of CNRS in Paris. I was renewed and finally able to be Director till 1994. In 1995, I have received another responsibility from the CNRS Administration, as Director of the CNRS French Research Group (GDR 1148) on solid-state laser type materials till 2002, gathering all French public and private laboratories working in this area.

I have continued my research activities at LPCML with strong national and international co-operations with Laboratories as mentioned in the following document. I was also a member of the National Committee for the Evaluation of the French Universities (CNE) (2003-2007), among 25 members for all academic fields in France.

My approach was to stimulate both fundamental and applied research on physical chemistry of inorganic luminescent materials with all members of the LPCML, by the conjugation of both, *elaboration techniques of luminescent materials, structural characterizations, spectroscopic analysis and tests of applications* with materials used for inorganic phosphors, laser materials and nonlinear crystals.

The elaboration of samples has been made in relationship with experts in chemistry either in France or abroad. The main polycrystalline phases have been prepared and characterized at LPCML and the oxide glassy phases have been synthetized at the Hebrew University of Jerusalem, at Saint-Gobain Company and at the Department of glass fluorides in Rennes. After 1983, we have spent a lot of efforts to find enough financial support to fixe new furnaces to grow single crystals.

The *crystal growth techniques* used were Czochralski (CZ), Laser Heated Pedestal Growth (LHPG), Floating crystal, µ-Pulling-Down which have been installed in LPCML. We have also established in 1996 a fruitful co-operation with the Fukuda's laboratory at the Tohoku University in Sendai (Japan) to get the best optical quality luminescent crystals we need mainly with laser crystals and nonlinear crystals. We have also worked in co-operation on nanocrystals and nanoceramics with Polish teams in Wroclaw (Poland).

The *Structural characterizations* are EPMA (Electron Probe Microscopy Analysis), X-ray Diffractometry, Small angle x-ray scattering, imaging confocal microscopy (ICM) and transmission electronic microscopy (TEM).

The *spectroscopic techniques* are transient and steady-state spectroscopic between 4K and 300K, like absorption, excitation, emission, decays of fluorescence in UV, visible, IR, by using CW and pulsed tunable laser sources.

spectroscopy techniques; Time-Resolved Spectroscopy, Site-selective

Spectroscopy, Fluorescence Line Narrowing Spectroscopy, Excites-State

Absorption, Two-Photon Absorption, Raman spectroscopy,

Thermoluminescence (10-600K)

Laser tests and *nonlinear generations* into pumping with lasers, laser- diodes and flash-lamps are made on the most promising materials.

We have investigated, by using the last mentioned spectroscopic tools, processes involved by up and down conversions, excited state dynamics, energy transfer mechanisms in materials which are doped by the following luminescent ions:

-heavy ions of ns^2 configuration like Bi^{3+} and Pb^{2+},

-metal transition ions of $3d^n$ configurations ($Ti^{3+, 4+}$, $Cr^{3+,4+,5+,6+}$, Mn $^{2+,3+,4+}$, Ni^{2+}, Co^{2+}, $V^{2+,3+}$).

-rare earth ions of $4f^n$ configurations (Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}).

The most important scientific programs were focused on the understanding of the excited state dynamics and relations between structures and optical properties in luminescent materials (polycrystals, glasses, glass-ceramics and now days nanomaterials and ceramics) :

1. Heavy ions: d^{10} s^2 configurations, Bi^{3+} and Pb^{2+} mercury-type ions

1.1. Spectroscopy and Excited state dynamics of Bi^{3+}-doped oxide materials

1.2. Spectroscopy and Excited state dynamics of Pb^{2+}-doped apatites

2. Transition metal ions: $3d^n$ configurations

2.1. Deep program on Cr^{3+}-doped crystals/glasses and related physical-chemistry questions

-Nucleation in Cr3+ ions-doped oxide glasses

-Cr3+ as a probe ion in garnets, magnetoplumbites, spinels, niobates

-Fano effect between 2E and 4T2 levels

-Model of Cr3+ multisites . Application to YAG, GGG, LuAG and (Ca,Zr)GGG garnets

-Effect of cation invertion in garnets on Cr3+ spectroscopy

-Four-Wave mixing technique applied to energy transfer of Cr3+ ions in garnets

-Laser spectroscopy of Cr3+-doped nonlinear niobate crystals, especially of stoichiometric and congruent LiNbO3

2.2. Other transition metal ions

-Ti3+,4+, Cr4+,5+,6+, Mn2+,3+,4+, Ni2+, Co2+, V2+,3+,spectroscopies

3. Rare earth ions: $4f^n$ configurations: Ce3+, Nd3+, Ho3+, Er3+, Tm3+, Yb3+

3.1.Especially a deep program on Yb^{3+}-doped Laser materials (main cooperation with Tohoku University, Japan)

YAG, GGG, LuAG, substituted GGG Garnets,

Y2O3, Sc2O3, Gd2O3, Lu2O3 sesquioxides,

MgAl2O4, ZnAl2O4 spinels,

KY3F10, CaF2 fluorides

- Yb3+- doped non cubic laser crystals

YAP perovskite,

KY(WO4)2, KGd(WO4)2 monoclinic tungstates

Apatites: a few compositions by µ-PD and Ca8La2(PO4)6O2 by CZ

- Yb3+- doped laser ceramics

Main advances on Yb3+ and other rare earth ions-doped laser materials: Figure-of-Merit, energy transfers, avalanche and looping mechanisms, concentration quenching mechanisms, gain model, optimization of laser, segregation of rare earth ions in ceramics

- Yb3+- laser glasses

3.2. Phosphors for white lighting

Ce3+/Eu2+/Eu3+-doped silicate glass phosphor and UV/blue LEDs as circadian response for white lighting.

3.3. Nanomaterials

Rare earth (Eu3+, Yb3+)-doped cubic/non-cubic nanomaterials (BaTiO3,YAG, spinels) and rare earth stoichiometric nanomaterials for luminescent concentrators in solar cells.

We have added other complementary techniques to the spectroscopic techniques which have lead to few pioneer results. A few examples are, RBS (Rutherford Back Scattering) channeling to locate the place of rare earth cations in $LiNbO_3$, SAXS (Small Angle X-ray Scattering) for the structural evolution of doped-xerogels during thermal treatments, TEM (Transmission Electronic Microscopy) to separate crystalline and glassy phases in optical glass-ceramics, and to detect phases at the grain boundaries and measurement of rare earth segregation in optical ceramics depending on the nature of the luminescent dopant, Imaging Confocal Microscopy (ICM) using fluorescence of Ce^{3+} in grains and grain boundaries of ceramics, EXAFS spectroscopy, EPR for characterization of transition metal ions.

3.4. Research of new optical transparent ceramis. Rare earth-doped cubic molybdate and tungstate compounds in cooperation with the University of Wroclaw (Poland)

3.5. Research of efficient fast scintillators. Evidence and XANES characterization of Ce^{4+} in Ce^{3+}-Mg^{2+}-co-doped garnet crystals. Cooperation with the Tohoku University (Japan).

3.6. Yb^{3+}-doped laser ceramics in cooperation with the Tohoku University

3.7. RE^{3+}-doped laser glasses

Strong cooperations with universities of Dourados and Maringa (Brazil), the Institute of Laser Engineering of Osaka (Japan) and SIOM in Shanghai (China)

Naturally, we have accompanied all theoretical and experimental results by using models already known but in a more creative way, from our personal ideas.

Main research activities are illustrated from the titles of both, the scientific articles published in peer reviewed journals, the oral communications presented in official international conferences and the PhD thesis I have supervised.