## PhD Scholarship in materials science, physical-chemistry, and engineering

Code Moyens-RH: **FR5-ADR1-LED**

Title: New generation of eco-efficient white LEDs: coupling of ZnO nanowire-based UV LEDs with lanthanide-free aluminium borate phosphors

Laboratories and researchers:

**LMGP** http://www.lmgp.grenoble-inp.fr/: D. Bellet, E. Appert, E. Sarigiannidou, V. Consonni
**Institut Néel** http://neel.cnrs.fr/: M. Salaun, E. Gautier-Luneau, A. Ibanez

Doctoral School: **I-MEP2**

Context of the PhD grant:

The PhD grant is associated with the IDEX (Institute of Excellence) at Grenoble and more specifically linked with the Cross Disciplinary Program Eco-SESA: "Eco-district: Safe, Efficient, Sustainable and Accessible energy". Based on observations at the building and neighbourhood levels, the Eco-SESA project aims to produce knowledge, concepts, tools and methods to rethink the planning, management and governance of urban energy systems and the design of their components. With a view to a safe, efficient, sustainable and accessible energy, these contributions will be shared with the scientific communities and the city and energy stakeholders. The Eco-SESA project will contribute to better taking into account the societal challenges of the energy transition, to extend the reputation of the Grenoble site to the social and human sciences, to increase the capacity to develop deployable innovations and, in so doing, to strengthen the international influence of the site. The integrated system approach is organized around 5 emerging research fronts to the convergence of scientific communities working on energy. Interdisciplinarity for instance between Material Sciences and Social & Human Sciences will be an important point in Eco-SESA since such interdisciplinarity will generate innovations. Therefore candidates will be selected with the following criteria: i/ excellence, ii/ strong motivation, iii/ appropriateness of candidate's competences with the proposed PhD project and iv/ the capacity of the candidate to work as well with other disciplines (than materials science) and to work in a cross-disciplinary context.
Grenoble is the second French research and innovation site after Paris and comes out as the best place in France to study.

Problematic & Context:

Light emitting diodes (LEDs) represent a technological breakthrough in the field of lighting. These solid-state devices offer low energy consumption (i.e. expected reduction of 50% of the global consumption related to lighting), long lifetimes and broad potentialities for programing and interfacing with numerical networks. However, their cost as well as the quality of the white light emission (i.e. strong emission in the blue) are major concerns both at the market and medical levels, limiting their development at a larger scale. The commercial devices are mainly based on LEDs composed of Ga and In (scarce and expensive elements) emitting in the blue (around 450 nm) or near UV (360-390 nm). These emissions are partly converted into the visible range by lanthanide-based phosphors (Ce, Eu, Tb), which are scarce, expensive and raise geopolitical concerns. Additionally, the synthesis processes require expensive, high-temperature physical and chemical deposition techniques. Importantly, the colour temperature and colour rendering index of LEDs are important to be considered and, especially their relationship with consumption habits (i.e. links between eye/visual comfort, cost, technology…) should more precisely be assessed to ensure the development of the LED market. Second, the remaining UV emissions raise medical questions for the eye safety, requiring complement medical investigations. Third, the recycling issue is crucial. All these parameters and issues directly affect the potential of the LED market via its multiple segmentation.

In this context, the development of eco-friendly, low-cost, and efficient white LEDs (WLEDs) producing comfortable and safe lighting for the eyes is essential and will be the topic of the present PhD thesis. These WLEDs will be composed of abundant and non-toxic elements, and will be produced through low-cost wet chemical techniques. It will consist in the combination of near UV LEDs made of ordered and doped ZnO nanowire (NW) arrays, prepared in LMGP Laboratory, with a new generation of lanthanides-free phosphors developed in Institut Néel. Semiconductor NWs are highly promising for the next generation of UV LEDs and offer numerous assets with respect to thin films thanks to their high surface to volume ratio: high crystalline quality, efficient stress relaxation favourable for hetero-epitaxy, efficient light extraction by waveguide effects [1,2]. ZnO is a direct wide band gap semiconductor of n-type, which is compatible with an UV emission around 375 nm at room temperature owing to its large exciton binding energy. It can further be grown with the NW shape by low-cost chemical bath deposition. Moreover, the combination of well-ordered heteroepitaxial ZnO NWs on p-type thin films of a direct wide band gap semiconductor lead to p-n heterojunctions, which are very relevant for the fabrication of UV LEDs. This promising type of LED is in strong development in LMGP [3]. To down-convert the near UV emitted light produced by these ZnO NW-based LEDs, a new family of lanthanide-free phosphors is being developed in Institut Néel. These original phosphors are amorphous aluminium borate powders, protected by a dedicated patent [4]. They have radical defects confined and stabilized in the glassy aluminium borate matrix, generating numerous intermediate energy levels in the band gap and thus broad photoluminescence bands in the visible part. It is thus possible to produce white light with an excellent colour rendering index between 92 and 94 [5,6]. The internal quantum efficiency is also very high (> 90%). However, their UV absorption is still limited, reducing the external quantum efficiency to 30%, which is promising but too low for real industrial applications, requiring the development of complementary works on syntheses and powder shaping.

## Main objectives and proposed work during the Thesis:

The main objectives of this PhD thesis will be to optimally combine near UV LEDs made of well-ordered arrays of doped ZnO NWs onto p-type GaN thin films with aluminium borate-based phosphors in order to maximize the luminescence efficiency of the resulting WLEDs. To this aim, the PhD student will work on the strongly correlated main three aspects: i) the optimisation of the emission wavelength of the near UV LEDs made of well-ordered arrays of doped ZnO NWs in LMGP by varying their diameter, length and period using advanced lithography as well as by inserting different doping elements [7], ii) the adjustment of the absorption wavelength of the aluminium borate-based phosphors and the improvement of their external quantum efficiency in Institut Néel by inserting transition metals or silicate groups as well as by varying grain size and shape through the monitoring of powder dispersion and densification, and iii) the integration of phosphors onto the near UV ZnO LEDs for the fabrication and characterization of WLEDs. The technological development will be based on fundamental knowledges related to chemical syntheses and to the characterization of the constituting elements (ZnO NWs, phosphors) so as to thoroughly monitor their intrinsic properties. Direct relationships will be established with Social & Human Sciences to estimate how the LED performances (colour temperature, colour rendering index, eye/visual comfort, cost, materials, technology, recycling issue…) can affect the potential of the LED market, for instance by changing the consumption habits. The investigation of the LED market will also be achieved to define the specifications associated with the different targeted applications (both at the indoor and outdoor levels and at different scales…).

## Proposed methods during the Thesis:

In the whole work of the present thesis, the PhD student will use different wet chemical deposition (films and NWs) or syntheses (phosphor powders) and several characterization techniques such as electron microscopy (SEM, TEM, STEM), X-ray diffraction, thermal and chemical analyses, UV-Vis-NIR spectrophotometry, granulometry, optical spectroscopy (photoluminescence, cathodoluminescence, thermoluminescence, electroluminescence, Raman spectroscopy…).

Keywords: UV-LEDs, ordered ZnO nanowires, doping, aluminium borate, phosphors

Collaborations & international opportunities:

In the framework of the present PhD thesis, a collaboration with the company «LED Engineering Development» will be established for the development of WLED prototypes. The PhD student will take part in the optimisation of these WLED devices to deduce the effects of the geometrical parameters. Additional international collaborations may be established with Swansea University, Institut Jaume Almera, University Federal de Goias, and University of Sao Paulo in Brazil.

Related references:

[1] Schmidt-Mende L., MacManus-Driscoll J.L., ***Materials Today*** 10 (2007) 40.
[2] Willander M., Nur O. *et al.* ***Nanotechnology*** 20 (2009) 332001.
[3] Consonni V., Sarigiannidou E., Appert E. *et al.* ***ACS Nano*** 8 (2014) 4761.
[4] PCT/EP2011/074032, Ext. intern. 2012-2014. A. Ibanez, V. Guimaraes, L.J.Q. Maia, A.C. Hernandes
[5] Guimaraes V.F., Ibanez A., Gautier-Luneau I. *et al.* ***J. Mater. Chem. C*** 3 (2015) 5795.
[6] Guimaraes V.F., Salaün M., Ibanez A., Gautier-Luneau I. *et al.* ***Solid State Sciences*** 65 (2017) 6.
[7] Verrier C., Appert E., Chaix-Pluchery, Rapenne L. *et al.* ***J. Phys. Chem. C*** 121 (2017) 3573.

Scientific environment: Located in the heart of an exceptional scientific environment, LMGP and Institut Néel offer the applicant a rewarding place to work. Moreover, the applicant will be integrated within a close collaboration between several scientists of LMGP, Institut Néel, IMEP-LaHC, and CEA laboratories as well as of G-SCOP, GAEL, and PACTE.

Profile: We are looking for a highly motivated student with outstanding or excellent Master's degree or equivalent qualification who is interested to work in an inter-disciplinary project. The main scientific cores are: materials science, physical-chemistry, and engineering. Interpersonal skills, dynamism, rigor and teamwork abilities will be appreciated. Candidates can be fluent either in English and/or in French.

Salary: According to French regulations for PhD

Application must be sent before the **1st of June 2017** in English or in French with the following:

- Curriculum vitae
- Cover letter
- Master thesis summary

Starting date for the scholarship: 1st September or October, 2017

Contacts: Mathieu Salaün: mathieu.salaun@neel.cnrs.fr; Tel: (33) 4 76 88 10 42
Vincent Consonni: vincent.consonni@grenoble-inp.fr; Tel: (33) 4 56 52 93 59
Daniel Bellet: daniel.bellet@phelma.grenoble-inp.fr; Tel: (33) 4 56 52 93 00
apply.eco-sesa@univ-grenoble-alpes.fr

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