Report from the stay of Prof. Martin Nikl in INO,CNR

<u>Period:</u> October 11 – 21 (9 working days)

<u>Program of the stay, activities performed:</u>

Experiments have been performed on the samples brought by M. Nikl: (i) ((Y,Lu)AG:Yb15% optical ceramics as laser; (ii) GaN-GaInN multiple quantum well, LuAG:Pr, GAGG:Ce and nonstoichiometric $SrHfO_3$-based ceramics as scintillators and (iii) multicomponent $(Na,K)LuS_2$-based and RE-doped termary sulfides as LED phosphor) at the INO laboratory. Characterization included time resolved luminescence spectroscopy, namely the photoluminescence decays in the extended time and dynamical scales, spectroscopic evaluation of timing characteristics at laser and scintillator materials.

The sample choice matched the planned visit program as a base for future collaboration:

(i) Laser materials based on the Yb doped hosts with broadband emission in the near infrared (e.g. multicomponent garnets) enabling the generation of ultrashort laser pulses.

(ii) Scintillating materials focused on the characteristics of rare earth-free ternary hafnates and ultrafast GaN-based multiple quantum well thin films which recently become a hot topic due to their exceptional properties.

(iii) Phosphors for LED lighting applications based on multicomponent sulfides providing widely tunable broadband spectra. Compositions without the use of Rare Earths Elements, to limit the current Chinese monopoly in their raw material supply.

Ad (i)

Multicomponent garnet host, due to atomistic local fluctuation of chemical composition imposes changes in the crystal field strength and site symmetry which might increase the bandwidth of Yb^{3+} emission and enable shorter fs pulse generation in the near infrared. We have continued in the spectroscopical characterization of (Y,Lu)AG:Yb15% ceramic samples prepared in collaborating laboratory in SICCAS, Shanghai, China, extending our recently published paper [A. Pirri, et al, *Spectroscopic and laser characterization of $Yb_{0.15}:(Lu_xY_{1-x})_3Al_5O_{12}$ ceramics with different Lu/Y balance.* Optics Express **24**, 17832-17842 (2016)]. It comes our that to achieve more enhanced effect on the Yb^{3+} emission spectra, more pronounced changes in the local composition are needed and mixed composition at all three cation sites, i.e. dodecahedral, octaheral and tetrahedral are needed. Based on the experience with the crystal growth of $Gd_3(Ga,Al)_5O_{12}$ crystals for fast scintillator in M. Nikl laboratory

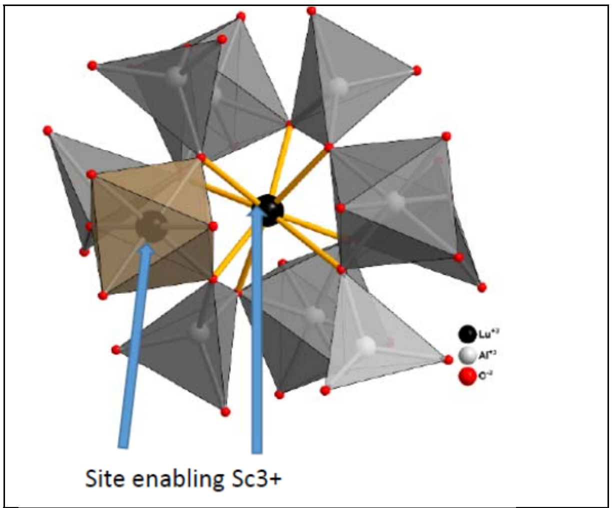

Fig. 1 The dodecahedral and octahedral sites enabling to introduce the Sc3+ dopant

(GAGG:Ce samples brought as fast scintillator) we decided to prepare the single crystal composition of $(Gd,Sc)_3$ $(Sc,Ga,Al)_5O_{12}$ doped by 5% of Yb^{3+} in the home laboratory of M. Nikl and deliver before the end of 2016 a designed optical element for laser test in INO laboratory. Sc is expected to occur in both the dodecahedral and octahedral sites, see Fig. 1, given the previous studies e.g. in Sc-admixed LuAG which will provide enhanced spread in local composition, crystal field and symmetry fluctuations, all beneficial to broaden Yb^{3+} emission spectra.

Ad (ii)

In the test of photoluminescence decays of scintillator samples the new excitation source built-up in INO laboratory, based on the 4^{th} harmonic of Nd:YAG laser (5 ns pulse with 1 mJ energy at 263 nm) was extensively tested.

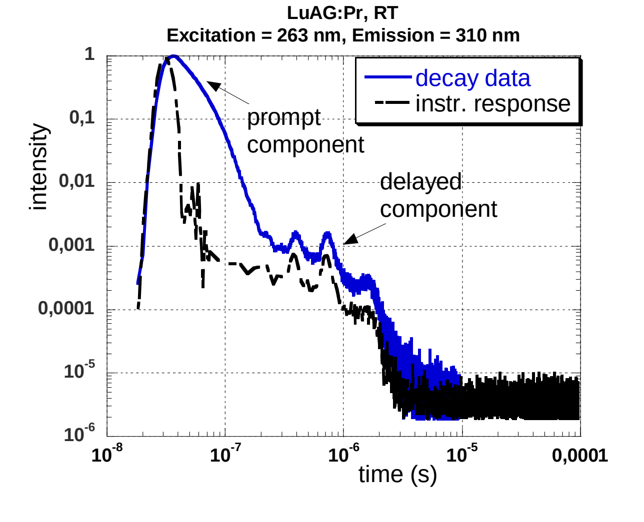

Fig. 2 Photoluminescence decay of LuAG:Pr excited by 263 nm laser pulse (4^{th} harmonic of Nd:YAG)

In the case of LuAG:Pr^{3+}, the excitation wavelength fits well the high energy wing of $4f\text{-}5d^1$ transition of Pr^{3+} which results in effective pumping of this emission center and its decay can be effectively measured, Fig. 2. Extreme dynamical resolution up to 5 orders of magnitude over exceptionally broad 1 ns – 10 µs time window enables to monitor simultaneously the prompt and delayed radiative recombination processes, the latter occurring due to interaction of electron in $5d^1$ excited state with the host (ionization, tunneling or similar processes).

In the case of GaN-GaInN multiple quantum well, characteristics emission spectra consist of fast exciton-based emission in violet-blue spectral region and a defect-based slow emission in the yellow spectral region.

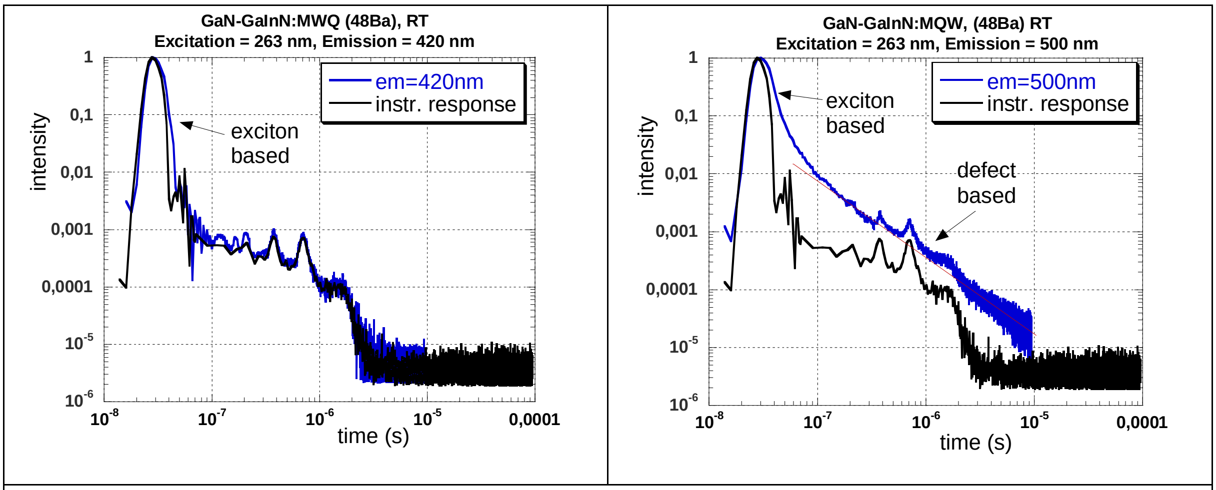

Fig. 3 Photoluminescence decay of GaN-GaInN MQW in the exciton (left) and defect (right) based emission bands.

Using the same experimental set-up as in the case of LuAG:Pr characteristic photoluminescence decays of both emission bands were obtained, Fig. 3. Indeed, the excitonic emission monitored at 420 nm shows only extremely fast decay component of about 2 ns decay time, while the decay at 500 nm (region where both excitonic and defect emission overlap) nicely show both the fast and slow decay process, the latter extending over 10 µs time scale. Straight course of the defect-based slow decay component might point to the existence of tunneling processes in the radiative recombination which will be the subject for future investigations.

From the experimental point of view, the origin of slow tail of the instrumental response was discussed. It might come partly from the photomultiplier after-peak process, but very probably also some effect due to electronic power supply circuits are not excluded. INO team will study further their origin as well as the stability of instrumental response over a time period of few hours which is necessary to know to estimate the jitters in the measured curves and their influence on the decay time evaluated from the convolution procedure (to be done in near future in home lab of M. Nikl).

Ad (iii)

In (K,Na)LuS2:Eu phosphor the tunable broad-band spectra over the visible region can be achieved by changing the ratio between K and Na, Fig. 4. Together with the broad excitation bands of Eu2+ in the near UV-blue region of spectra it appears very promising for construction of circadian sources for smart solid state lighting sources.

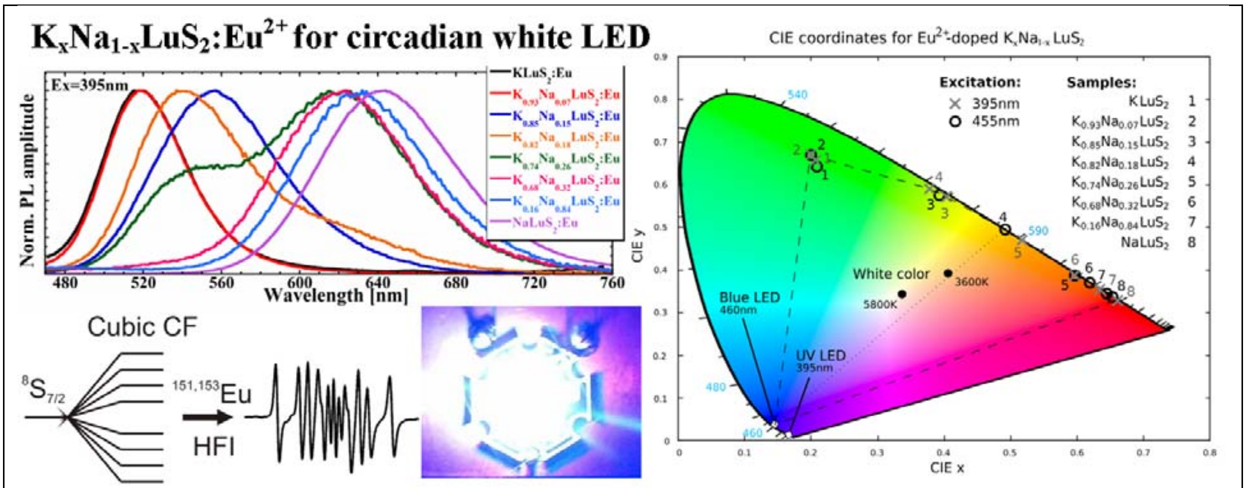

Fig. 4 Photoluminescence spectra of (K,Na)LuS2:Eu2+ phosphor (upper left), related CIE diagram (right), level splitting of Eu^{2+} paramagnetic center monitored by EPR (lower left) and lighting element (excitation by 455 nm blue LED) constructed with the phosphor (lower central).

We have concentrated on the test of photoluminescence decays of these phosphors under 263 nm pulse laser excitation to explore parasitic emission processes from the host which might negatively influence the efficiency of these phosphors. The band occurring in violet-blue spectral region was found and inspected, Fig. 5.

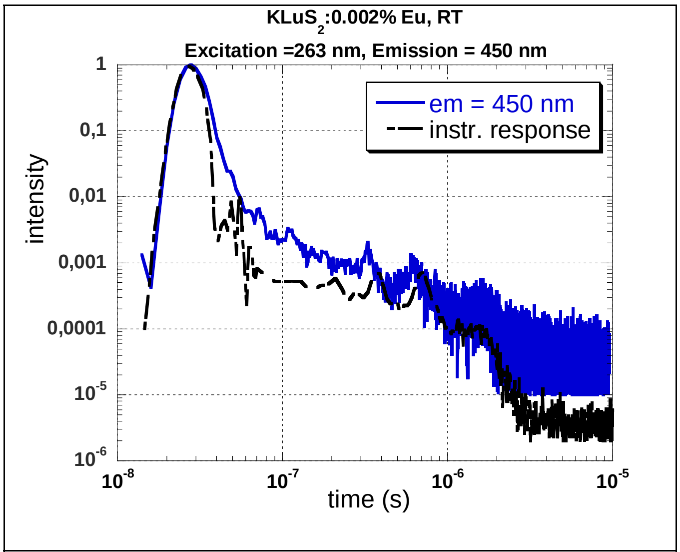

Fig. 5 Photoluminescence decay of KLuS2:Eu

In the discussions during the stay of M. Nikl the possibilities for the project proposals at EC level (H2020 programs, in particular ICT calls), COST actions and other funding opportunities were judged as well as possible synergies with ongoing national programs. We decided to participate jointly in the proposal under preparation in INO group focused on the solid state lighting based on organic LED materials (**Nuovi promettenti coloranti organici per illuminazione civile**) where competencies of both groups suitably complement.

M. Nikl delivered two talks in the INO group focused on the recent R&D trends and research activities in IP-CAS on scintillators and phosphors for white LED lighting the pdf copies of which were provided to INO group for further information and discussion.

As for organization of the stay, I am pleased to say that all the aspects of the stay were perfectly prepared and we achieved in less then two weeks a number of experimental results, progress in the experimental set-up development, and several ideas for future collaboration have been defined and are under continued discussion.

In Sesto Fiorentino, October 21, 2016 Martin Nikl

The proposer of the CNR Short Term Mobility visit , Matteo Vannini